

PTO

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 089 125 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
04.04.2001 Bulletin 2001/14

(51) Int. Cl.⁷: G03C 11/14, G03C 11/08

(21) Application number: 00203195.3

(22) Date of filing: 14.09.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: 30.09.1999 US 408605

(71) Applicant: EASTMAN KODAK COMPANY
Rochester, New York 14650 (US)

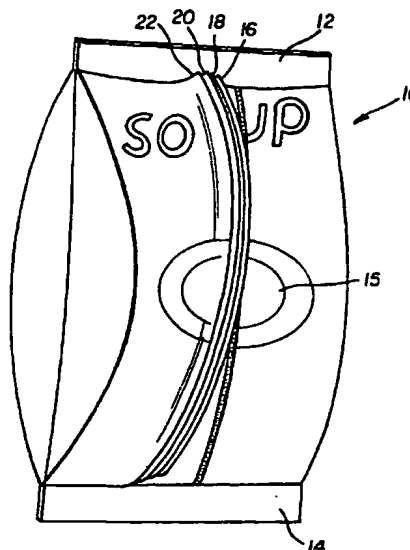
(72) Inventors:
• Bourdelais, Robert Paul,
Eastman Kodak Company
Rochester, New York 14650-2201 (US)

• Aylward, Peter Thomas,
Eastman Kodak Company
Rochester, New York 14650-2201 (US)
• Camp, Alphonse Dominic,
Eastman Kodak Company
Rochester, New York 14650-2201 (US)
• Gula, Thaddeus Stephen,
Eastman Kodak Company
Rochester, New York 14650-2201 (US)

(74) Representative:
Nunney, Ronald Frederick Adolphe et al
Kodak Limited,
Patents, W92-3A,
Headstone Drive
Harrow, Middlesex HA1 4TY (GB)

(54) Flexible silver halide packaging material

(57) The invention relates to an element consisting essentially of a transparent polymer sheet, at least one emulsion adhering layer, and at least one light sensitive silver halide grain containing emulsion layer adhered to said emulsion adhering layer, wherein said polymer sheet is less than 40 μm in thickness.

**FIG. 1**

EP 1 089 125 A1

Description

FIELD OF THE INVENTION

5 [0001] The invention relates to packaging materials. In a preferred form it relates to the use of silver halide for the printing of text, graphics, and images onto packaging material.

BACKGROUND OF THE INVENTION

10 [0002] Glue applied labels are adhered to packages to build brand awareness, show the contents of the package, convey a quality message regarding the contents of a package, and supply consumer information such as directions on product use, or an ingredient listing of the contents. Printing is also applied to packaging materials that will form the final consumer package. An example is a fried snack package that typically contains several functional layers that provide package strength and an incorporated oxygen barrier to prevent oxidation of the residual frying oils. Printing is typically
15 applied directly to the label utilizing gravure printing or flexography. The three types of information printed on a label media are text, graphic, and images. Some packages only require one type of information, while other packages require all three types of information.

[0003] Flexography is an offset letterpress technique where the printing plates are made from rubber or photopolymers. The flexography printing is accomplished by the transfer of ink from the raised surface of the printing plate to the
20 surface of the material being printed. The rotogravure method of printing uses a print cylinder with thousands of tiny cells which are below the surface of the printing cylinder. The ink is transferred from the cells when the print cylinder is brought into contact with the material to be printed at the impression roll. Printing inks for flexography or rotogravure include solvent-based inks, water-based inks, and radiation cured inks. While rotogravure and flexography printing does provide acceptable image quality, these two printing methods require expensive and time-consuming preparation of
25 print cylinders or printing plates which make printing jobs of less than 100,000 units expensive as the setup cost, and the cost of the cylinders and printing plates is typically depreciated over the size of the print job.

[0004] Recently, digital printing has become a viable method for the printing of information on packages. The term "digital printing" refers to the electronic digital characters or electronic digital images that can be printed by an electronic output device capable of translating digital information. The two main digital printing technologies are ink jet and electrophotography.
30

[0005] The introduction of piezo impulse drop-on-demand (DOD) and thermal DOD ink jet printers in the early 1980's provided ink jet printing systems. These early printers were very slow, and the ink jet nozzles often clogged. In the 1990's Hewlett Packard introduced the first monochrome ink jet printer, and, shortly thereafter, the introduction of color, wide format ink jet printers enabled businesses to enter the graphic arts market. Today, a number of different ink
35 jet technologies are being used for packaging, desktop, industrial, commercial, photographic, and textile applications.

[0006] In piezo technology, a piezo crystal is electrically simulated to create pressure waves, which eject ink from the ink chamber. The ink can be electrically charged and deflected in a potential field, allowing the different characters to be created. More recent developments have introduced DOD multiple jets that utilize conductive piezo ceramic material which, when charged, increases the pressure in the channel and forces a drop of ink from the end of the nozzle.
40 This allows for very small droplets of ink to form and be delivered at high speed at very high resolution, approximately 1,000 dpi printing.

[0007] Until recently, the use of color pigments in jet inks was uncommon. However, this is changing rapidly. Sub-micron pigments were developed in Japan for ink jet applications. Use of pigments allows for more temperature resistant inks required for thermal ink jet printers and laminations. Pigmented water-based jet inks are commercially
45 available, and UV-curable jet inks are in development. Pigmented inks have greater lightfastness and water-resistance.

[0008] Digital ink jet printing has the potential to revolutionize the printing industry by making short-run, color print jobs more economical. However, the next commercial stage will require significant improvements in ink jet technology; the major hurdle remaining is to improve print speed. Part of this problem is the limitation of the amount of data the printer can handle rapidly. The more complex the design, the slower the printing process. Right now they are about ten
50 times slower than comparable digital electrostatic printers.

[0009] Electrophotography was invented in the 1930's by Chester Carlson. By the early 1970's, the development of an electrophotographic color copier was being investigated by many companies. The technology for producing color copiers was already in place, but the market was not. It would take many more years until customer demand for color copies would create the necessary incentive to develop suitable electrostatic color copiers. By the late 1970's a few
55 companies were using fax machines that could scan a document, reduce the images to electronic signals, send them out over the telephone wire and, using another fax machine, retrieve the electronic signals and print the original image using heat-sensitive papers to produce a printed copy.

[0010] In 1993 Indigo and Xeikon introduced commercial digital printing machines targeted on short-run markets

that were dominated by sheet-fed lithographic printers. Elimination of intermediate steps associated with negatives and plates used in offset printing provides faster turnaround and better customer service. These digital presses share some of the characteristics of traditional xerography but use very specialized inks. Unlike inks for conventional photocopiers, these inks are made with very small particle size components in the range of 1 μm . Dry toners used in xerography are typically 8-10 μm in size.

[0011] In 1995 Indigo introduced the Ominus press designed for printing flexible packaging products. The Ominus uses a digital offset color process called One Shot Color that has six colors. A key improvement has been the use of a special white Electroink for transparent substrates. The Ominus web-fed digital printing system allows printing of various substrates using an offset cylinder that transfers the color image to the substrate. In principle, this allows perfect register regardless of the substrate being printed; paper, film, and metal can be printed by this process. This digital printing system is based on an electrophotographic process where the electrostatic image is created on the surface of a photoconductor by first charging the photoconductor by charge corona and exposing the photoconductive surface to a light source in image fashion.

[0012] The charged electrostatic latent image is then developed using ink containing an opposite charge to that on the image. This part of the process is similar to that of electrostatic toners associated with photocopying machines. The latent charged electrostatic image formed on the photoconductor surface is developed by means of electrophoretic transfer of the liquid toner. This electrostatic toner image is then transferred to a hot blanket, which coalesces the toner and maintains it in a tacky state until it is transferred to the substrate, which cools the ink and produces a tack-free print.

[0013] Electroinks typically comprise mineral oil and volatile organic compounds below that of conventional offset printing inks. They are designed so that the thermoplastic resin will fuse at elevated temperatures. In the actual printing process, the resin coalesced, the inks are transferred to the substrate, and there is no need to heat the ink to dry it. The ink is deposited on the substrate essentially dry, although it becomes tack-free as it cools and reaches room temperature.

[0014] For several decades a magnetic digital technology called "magnetography" has been under development. This process involves creating electrical images on a magnetic cylinder and using magnetic toners as inks to create the image. The potential advantage of this technology lies in its high press speed. Tests have shown that speeds of 200 meters per minute. Although these magnetic digital printers are limited to black and white copy, developments of color magnetic inks would make this high-speed digital technology economically feasible. The key to its growth will be further development of the VHSM (very high speed magnetic) drum and the color magnetic inks.

[0015] Within the magnetic digital arena, a hybrid system called magnetolithography has been built and tested on narrow web and short-run applications developed by Nipson Printing Systems in Belfort, France. The technology appears to provide high resolution, and tests have been conducted using a silicon-based, high density magnetographic head. Much more work is necessary in the ink development to bring this system to a competitive position relative to ink jet or electrophotography. However, the fact that it has high speed printing potential makes it an attractive alternate for packaging applications in which today's ink jet and electrophotography technologies are lagging.

[0016] Photographic materials have been known for use as prints for preserving memories for special events such as birthdays and vacations. They also have been utilized for large display materials utilized in advertising. These materials have been known as high quality products that are costly and somewhat delicate as they would be easily defaced by abrasion, water, or bending. Photographs are traditionally placed in frames, photo albums, and behind protective materials in view of their fragile and delicate nature, as well as their value. They are considered luxury items for the consumers to preserve a record of important events in their lives. They also have been considered as expensive display materials for advertising. In view of their status as luxury items, they have not been utilized in other areas of commerce.

PROBLEM TO BE SOLVED BY THE INVENTION

[0017] There is a need for printed information on packages that is high in quality and, at the same time, economical for short runs, as well as a printing method that can print from digital information files.

SUMMARY OF THE INVENTION

[0018] It is an object of the invention to provide higher quality images to packaging materials.

[0019] It is another object to provide a packaging material having good running properties and low friction for use in high speed packaging machines.

[0020] It is a further object to provide a silver halide imaging system that can be exposed using a conventional negative working optical system and exposed using optical digital printing systems.

[0021] These and other objects of the invention are accomplished by an element consisting essentially of a transparent polymer sheet, at least one emulsion adhering layer, and at least one light sensitive silver halide grain containing emulsion layer adhered to said emulsion adhering layer, wherein said polymer sheet is less than 40 μm in thickness.

ADVANTAGEOUS EFFECT OF THE INVENTION

[0022] The invention provides improved image quality for packaging materials. It particularly provides a printing method that can print text, graphic and images using negative working optical systems or optical digital printing systems.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023]

Fig. 1 is an illustration of the structure of an imaged silver halide packaging material formed into a filled bag.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The invention has numerous advantages over prior practices in the art. Recently there has been a trend in the marketing of mass consumer items to try to localize the marketing to separately approach smaller groups. These groups may be regional, ethnic, gender, age, or special interest differentiated. In order to approach these different groups, there is a need to provide packaging that is specifically directed to these groups. As discussed above, the traditional packaging materials are generally suited for very long runs of material and to form shorter runs or to provide rapid changes in packaging is impossible or very expensive. Simultaneously with this need for low cost short run packaging materials, we have found silver halide based photographic materials that are suitable for packaging uses. Further, recently there has become available rapid photo processing apparatus suitable for short runs of material. There is also available silver halide processing apparatus that is capable of high speed relatively long continuous runs of material. The combination of low cost packaging suitable photographic material with the processing apparatus available for rapid short and long runs of material has resulted in the opportunity for silver halide material to be utilized in packaging materials. Silver halide materials that have properties such as flexibility, low cost, and the ability to flex and bend has resulted in materials satisfactory and suitable for packaging.

[0025] The utilization of the thin, flexible, and tough silver halide materials results in a packaging material having many superior properties. These materials are capable of having brighter, sharper, and higher color images that anything presently available in packaging. The packaging materials of the invention have a depth of image unsurpassed by existing packaging materials. The packaging materials of the invention may be further provided with a variety of packing materials that are suitable for various packaging needs, such as ultrasonic sealing, cold sealing, hot sealing, folding, and glue sealing. The packaging materials of the invention while having the advantage of superior image are available on thin base materials which are low in cost while providing superior opacity and strength. The packaging materials of the invention as they may be imaged by flash optical exposure or digital printing have the ability to be formed in short runs and to be rapidly switched from one image to the next without delay.

[0026] The silver halide imaging materials of the invention allows packages to be rapidly designed and brought to market. For instance, significant events in sports or entertainment may be practically instantly brought to market as a digital image may be immediately flash exposed onto packaging materials and utilized within moments from the time of the event. This is in contrast to typical photogravure or flexographic imaging where lead times are typically several weeks. Further, the quality of the silver halide formed image lends itself to collectable images formed as a part of packaging much better than previous images which were of lower quality and were less desirable for collecting. Finally, the regional customization of images is rapidly possible.

[0027] The ability to rapidly change packaging also would find use in the need to provide regional labeling with different languages and marketing themes in different countries. Further, different countries have different legal labeling requirements as to content. For instance, alcoholic beverages such as wine and beer are subject to a wide variety of regional and national variations in labeling requirements. Wines manufactured in France may have long delays in shipping out of France due to the wait for national labeling in other countries. Photographic images also would be particularly desirable for premium products such as fine wines, perfumes, and chocolates, as they would be of high quality and reflect the high quality of the product-in the package.

[0028] The invention provides a printing method that is economically viable when printing short runs as the cost of printing plates or printing cylinders are avoided. The use of silver halide images applied to a package ensures the highest image quality currently available compared to a six color rotogravure printing material. Further, because the yellow, magenta and cyan layers contain gelatin inter layers, the silver halide images appear to have depth compared to ink jet or electrophotographic images which appear flat and lifeless. Silver halide image layers have also been optimized to accurately replicate flesh tones, providing superior images of people compared to alternate digital imaging technologies.

[0029] Silver halide image technology can simultaneously print text, graphics and photographic quality images on

the same package. Since the silver halide imaging layers of the invention are digitally compatible, text, graphics and images can be printed using known digital printing equipment such as lasers and CRT printers. Because the silver halide system is digitally compatible, each package can contain different data enabling customization of individual packages without the extra expense of printing plates or cylinders. Further, printing digital files allows the files to be transported using electronic data transfer technology such as the internet thus reducing the cycle time to apply printing to a package. Silver halide imaging layers can be digitally exposed with a laser or CRT at speeds greater than 75 meters per minute allowing competitive printing speeds compared to current ink jet or electrophotographic printing engines. These and other advantages will be apparent from the detailed description below.

[0030] The terms as used herein, "top", "upper", "emulsion side", and "face" mean the side or toward the side of a photographic label bearing the imaging layers. The terms "base sheet" mean the side or toward the side of the photographic label or photographic packaging material opposite from the side bearing the photosensitive imaging layers or developed image.

[0031] The term as used herein, "transparent" means the ability to pass radiation without significant deviation or absorption. For this invention, "transparent" material is defined as a material that has a spectral transmission greater than 90%. For a photographic element, spectral transmission is the ratio of the transmitted power to the incident power and is expressed as a percentage as follows; $T_{RGB} = 10^{-D} \cdot 100$ where D is the average of the red, green and blue Status A transmission density response measured by an X-Rite model 310 (or comparable) photographic transmission densitometer.

[0032] In order to provide a digital printing technology that can be applied to a package that is high in quality, can handle text, graphic and images, is economical for short run printing jobs and accurately reproduce flesh tones, silver halide imaging is preferred. The silver halide technology can be either black and white or color. The silver halide imaging layers coated on a thin flexible polymer base sheet are preferably exposed and developed prior to lamination to a bottom sheet forming a photographic label. The thin flexible base sheet of the invention contains the necessary tensile strength properties and coefficient of friction properties to allow for efficient transport and application of the images in high speed packaging equipment. Further, the thin flexible base sheet of the invention preferably contains barrier properties critical for packaging applications that require moisture barrier, oxygen barrier or a organoleptic barrier. The transparent polymer sheet preferable contains an integral blue tinted layer to offset the native yellowness of the gelatin used in the silver halide emulsion. By compensating for the yellowness of the gelatin, a desirable neutral white in the density minimum areas of the image is achieved.

[0033] By applying the light sensitive silver halide imaging layers to a thin, transparent polymer sheet, developing the image and adhering a base sheet, the imaging layers which are typically formed in a gelatin binder are protected from environmental solvents such as water, cleaning solutions are coffee. Further, the thin polymer sheet of the invention is scratch resistant protecting the delicate imaging layers from handling induced damage to the imaging layers.

[0034] Applying the light sensitive silver halide imaging layers to the thin, transparent polymer sheet of the invention, allows for a variety of base sheets to be utilized after image development eliminating problems associated with applying the imaging layers to the entire packaging material. An example would be chemistry that is typically applied to the base sheet for oxygen barrier properties tends to interfere with the silver halide imaging chemistry resulting is a undesirable chemical development of the light sensitive silver grains. By applying the developed imaging layers coated on the thin polymer sheet to the base sheet, a wider range of oxygen barrier chemistry can be utilized thereby increasing the commercial value of the photographic label.

[0035] For the photographic packaging material of this invention the light sensitive emulsion layer is coated onto thin, transparent polymer sheet with an emulsion adhesion layer. This photographic packaging material can then be printed with images using conventional exposure technology and processed using traditional photographic chemistry. When the thin transparent biaxially oriented sheet with the developed image is adhered to the base material, encapsulating the imaging layers between the thin, transparent polymer sheet and the base sheet, a photographic reflective label material is created with the thin, transparent polymer sheet providing protection to the emulsion layer. The biaxially oriented polymer sheet is thin, preferably less than 40 micrometers. A thin biaxially oriented sheet has the advantage of allowing longer rolls of light sensitive silver halide coated rolls compared with applying the light sensitive silver halide coating to the entire label structure. The thin polymer sheets also significantly reduces shipping cost of developed images as the thin polymer sheet of the invention weight significantly less than prior art photographic paper. A thin sheet is also necessary to reduce unwanted reduction in the transparency of the polymer sheet resulting in a cloudy image as the thin, transparent polymer sheet is laminated to a reflective support.

[0036] The preferred optical transmission for the thin, flexible polymer sheet is between 90% and 100%. Below 86% optical transmission the image quality is reduced as light must be either reflected through the back of the photographic label in the case of a clear photographic label reducing the amount of light reaching an observers eye. Or light must be reflected from the opaque photographic label base, reducing the amount of light reaching the observers' eye. In both cases, the image appears undesirably cloudy and dark.

[0037] Another unique feature of this invention is the elimination of an antihalation layer to the imaging layers. Typ-

ically, an antihalation layer prevents unwanted secondary exposure of the silver crystals in the imaging layer as light is absorbed in the antihalation layer during exposure. The prevention of secondary exposure of the light sensitive silver crystals, will significantly increase the sharpness of the image. Unexpectedly, it was found that acceptable image quality can be obtained during the digital exposure of the silver halide imaging layers without the need for an antihalation layer.

Surprisingly, it has also been found that polymer chemistry can be added to the biaxially oriented polymer sheet to provide ultraviolet protection to the couplers used in the image layer without reducing the quality of the silver halide formed image. Traditionally prior art photographic print required UV protection in the gelatin overcoat layer. The incorporation of the ultraviolet protection materials in the transparent polymer sheet of this invention provides more efficient ultraviolet protection to the UV sensitive imaging color couplers and is lower in cost as less ultraviolet filter materials are required in the polymer sheet than in a gelatin overcoat.

[0038] Illustrated in Fig. 1 is a silver halide packaging material formed into a bag suitable for packaging dry soup or fried food such as potato chips. The silver halide packaging bag 10 is formed into a cylinder utilizing a forming collar. A cross seal (not shown) is created to maintain the integrity of the cylinder. The ends of the cylinder are sealed at 12 and 14 to create an enclosed bag. The web material used to form the bag comprises a transparent polymer sheet 22, developed silver halide imaging layers 20, a pressure sensitive adhesive 18 and a base sheet 16.

[0039] Suitable thin, transparent polymer sheets for the coating of the silver halide imaging must not interfere with the light sensitive silver halide imaging layers utilized in this invention. Further the polymer sheet needs to be flexible and tough to withstand the rigors of high speed packaging equipment and handling of the package by retailers and consumers. Biaxially oriented polymer sheets are preferred and manufactured by coextrusion of the sheet, which may contain several layers, followed by biaxial orientation. Such biaxially oriented sheets are disclosed in, for example, U.S. Pat. No. 4,764,425. Biaxially oriented sheet are preferred as the orientation process produces a thin, tough transparent polymer sheet that has an acceptable surface for the application of silver halide imaging layers.

[0040] Preferred classes of thermoplastic polymers for the flexible tough polymer sheet include polyolefins, polyesters, polyamides, polycarbonates, cellulosic esters, polystyrene, polyvinyl resins, polysulfonamides, polyethers, polyimides, polyvinylidene fluoride, polyurethanes, polyphenylenesulfides, polytetrafluoroethylene, polyacetals, polysulfonates, polyester ionomers, and polyolefin ionomers. Copolymers and/or mixtures of these polymers can be used.

[0041] Polyolefins particularly polypropylene, polyethylene, polymethylpentene, and mixtures thereof are preferred for the flexible, tough polymer sheet. Polyolefin copolymers, including copolymers of propylene and ethylene such as hexene, butene and octene are also preferred. Polypropylenes are most preferred because they are low in cost and have good strength and surface properties.

[0042] Preferred polyesters for the thin, flexible polymer sheet of the invention include those produced from aromatic, aliphatic or cycloaliphatic dicarboxylic acids of 4-20 carbon atoms and aliphatic or alicyclic glycols having from 2-24 carbon atoms. Examples of suitable dicarboxylic acids include terephthalic, isophthalic, phthalic, naphthalene dicarboxylic acid, succinic, glutaric, adipic, azelaic, sebacic, fumaric, maleic, itaconic, 1,4-cyclohexanedicarboxylic, sodiumsulfisophthalic and mixtures thereof. Examples of suitable glycols include ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, 1,4-cyclohexanedimethanol, diethylene glycol, other polyethylene glycols and mixtures thereof. Such polyesters are well known in the art and may be produced by well-known techniques, e.g., those described in U.S. Pat. Nos. 2,465,319 and 2,901,466. Preferred continuous matrix polyesters are those having repeat units from terephthalic acid or naphthalene dicarboxylic acid and at least one glycol selected from ethylene glycol, 1,4-butanediol and 1,4-cyclohexanedimethanol. Poly(ethylene terephthalate), which may be modified by small amounts of other monomers, is especially preferred. Other suitable polyesters include liquid crystal copolyesters formed by the inclusion of suitable amount of a co-acid component such as stilbene dicarboxylic acid. Examples of such liquid crystal copolyesters are those disclosed in U.S. Pat. Nos. 4,420,607; 4,459,402; and 4,468,510.

[0043] Useful polyamides for the thin, flexible polymer sheet include nylon 6, nylon 66, and mixtures thereof. Copolymers of polyamides are also suitable continuous phase polymers. An example of a useful polycarbonate is bisphenol-A polycarbonate. Cellulosic esters suitable for use as the continuous phase polymer of the composite sheets include cellulose nitrate, cellulose triacetate, cellulose diacetate, cellulose acetate propionate, cellulose acetate butyrate, and mixtures or copolymers thereof. Useful polyvinyl resins include polyvinyl chloride, poly(vinyl acetal), and mixtures thereof. Copolymers of vinyl resins can also be utilized.

[0044] Because light sensitive silver halide emulsions, typically coated in gelatin do not adhere well to polymer substrates, an integral emulsion adhesion layer is desired to eliminate the need for expensive primer coatings. In a preferred embodiment of the invention, the flexible, transparent polymer sheet is provided with an integral silver halide emulsion adhesion layer. The total thickness of the integral emulsion adhesion layer should be between 0.20 micrometers and 1.5 micrometers, preferably between 0.5 and 1.0 micrometers. Below 0.5 micrometers any inherent non-planarity in the coextruded skin layer may result in unacceptable color variation. At thickness greater than 1.0 micrometers, there is little benefit in the photographic optical properties such as image resolution. At thickness greater than 1.0 micrometers there is also a greater material volume to filter for contamination such as clumps, poor color pigment dispersion, or contami-

nation.

[0045] Addenda may be added to the flexible, transparent polymer sheet to change the color of the imaging element. For a photographic label, a transparent polymer sheet with a slight bluish tinge is preferred. The addition of the slight bluish tinge may be accomplished by any process which is known in the art including the machine blending of color concentrate prior to extrusion and the melt extrusion of blue colorants that have been pre-blended at the desired blend ratio. Colored pigments that can resist extrusion temperatures greater than 320°C are preferred, as temperatures greater than 320°C are necessary for coextrusion of the skin layer. Blue colorants used in this invention may be any colorant that does not have an adverse impact on the imaging element. Preferred blue colorants include Phthalocyanine blue pigments, Chromophthal blue pigments, Irgazin blue pigments, Irgalite organic blue pigments, and pigment Blue 60.

[0046] The preferred integral emulsion adhesion layer for the flexible, transparent polymer sheet is polyethylene. Polyethylene is relative easy to co extrude and orient. Gelatin based light sensitive silver halide imaging layers also adhere well to polyethylene after a corona discharge treatment prior to emulsion coating. This avoids the need for expensive emulsion adhesion promoting coating from being applied to obtain acceptable emulsion adhesion between the biaxially oriented sheets of this invention and the image forming layers.

[0047] The preferred thickness of the flexible, transparent polymer sheet of this invention is between less than 40 micrometers. A polymer sheet above 45 micrometers offers no benefit to the silver halide imaging layer and does not offer any additional protection against handling damage and, therefore, does not justify the additional expense for the additional material. The most preferred thickness for the thin, transparent polymer sheet is between 10 and 20 micrometers. Below 6 micrometers the web is difficult to convey through manufacturing and the photographic printers.

[0048] The coefficient of friction or COF of the flexible, transparent polymer sheet containing the silver halide imaging layer is an important characteristic as the COF is related to conveyance and forming efficiency in automated labeling equipment. COF is the ratio of the weight of an item moving on a surface to the force that maintains contact between the surface and the item. The mathematical expression for COF is as follows:

$$\text{COF} = \mu = (\text{friction force} / \text{normal force})$$

[0049] The COF of the flexible, transparent polymer sheet is measured using ASTM D-1894 utilizing a stainless steel sled to measure both the static and dynamic COF of the flexible, transparent polymer sheet. The preferred COF for the flexible, transparent polymer sheet of the invention is between 0.2 and 0.6. As an example, a 0.2 COF is necessary for coating on a label used in a pick-and-place application. The operation using a mechanical device to pick a label and move it to another point requires a low COF so the label will easily slide over the surface of the label below it. At the other extreme, large sheets such as book covers require a 0.6 COF to prevent them from slipping and sliding when they are piled on top of each other in storage. Occasionally, a particular material may require a high COF on one side and a low COF on the other side. Normally, the base material itself, such as a plastic film, foil, or paper substrate, would provide the necessary COF for one side. Application of an appropriate coating would modify the image side to give the higher or lower value. Conceivably, two different coatings could be used with one on either side.

[0050] COF can be static or kinetic. The coefficient of static friction is the value at the time movement between the two surfaces is ready to start but no actual movement has occurred. The coefficient of kinetic friction refers to the case when the two surfaces are actually sliding against each other at a constant rate of speed. COF is usually measured by using a sled placed on the surface. The force necessary at the onset of sliding provides a measurement of static COF. Pulling the sled at a constant speed over a given length provides a measure of kinetic frictional force.

[0051] The preferred modulus of elasticity for the flexible, transparent polymer sheet, an emulsion adhering layer and the light sensitive silver halide imaging layers is between 1,200 MPa and 7,000 MPa. Below 800 MPa, the thin, flexible transparent polymer sheet is difficult to transport in manufacturing and imaging development equipment. Further, below 600 MPa, the photographic label material begins to fail in bursting strength tests that are done in gas filled snack bags for example. Above 8,000 MPa, there is little improvement in the integrity of the package and, therefore, not cost justified. Elastic modulus of the flexible, transparent is measured using procedure ASTM D882A.

[0052] These flexible, transparent polymer sheets may be coated or treated after the coextrusion and orienting process or between casting and full orientation with any number of coatings which may be used to improve the properties of the sheets including printability, to provide a vapor barrier, to make them heat sealable, or to improve the adhesion to the support or to the photo sensitive layers. Examples of this would be acrylic coatings for printability and a coating of polyvinylidene chloride for heat seal properties. Further examples include flame, plasma or corona discharge treatment to improve printability or adhesion.

[0053] A base sheet is utilized in the invention to encapsulate the delicate developed silver halide imaging layers. The base sheet is applied to the developed silver halide imaging layers to provide whiteness because in a silver halide system, the color white can not yet be created with dye couplers. Therefore, the whiteness of the base creates white in the image density minimum areas. The base sheet also provides stiffness, barrier properties and a surface for the application of an adhesive for adhesion to a package. Further, suitable base sheets for lamination to the silver halide imaging

layers needs to be flexible and tough to withstand the rigors of high speed packaging equipment and handling of the package by retailers and consumers. Biaxially oriented polymer sheets are preferred for the base sheet and manufactured by coextrusion of the sheet, which may contain several layers, followed by biaxial orientation. Such biaxially oriented sheets are disclosed in, for example, U.S. Pat. No. 5,866,282 (Bourdelaïs et al.). Biaxially oriented polymer sheets are preferred as the orientation process produces a thin, tough transparent polymer sheet that has the required mechanical characteristic to withstand the rigors of a high speed packaging equipment.

[0054] Preferred classes of thermoplastic polymers for the base sheet include polyolefins, polyesters, polyamides, polycarbonates, cellulosic esters, polystyrene, polyvinyl resins, polysulfonamides, polyethers, polyimides, polyvinylidene fluoride, polyurethanes, polyphenylenesulfides, polytetrafluoroethylene, polyacetals, polysulfonates, polyester ionomers, and polyolefin ionomers. Copolymers and/or mixtures of these polymers can be used.

[0055] Polyolefins particularly polypropylene, polyethylene, polymethylpentene, and mixtures thereof are preferred for the flexible, tough polymer sheet. Polyolefin copolymers, including copolymers of propylene and ethylene such as hexene, butene, and octene are also preferred. Polypropylenes are most preferred because they are low in cost and have good strength and surface properties.

[0056] Preferred polyesters for the base sheet of the invention include those produced from aromatic, aliphatic or cycloaliphatic dicarboxylic acids of 4-20 carbon atoms and aliphatic or alicyclic glycols having from 2-24 carbon atoms. Examples of suitable dicarboxylic acids include terephthalic, isophthalic, phthalic, naphthalene dicarboxylic acid, succinic, glutaric, adipic, azelaic, sebacic, fumaric, maleic, itaconic, 1,4-cyclohexanedicarboxylic, sodiumsulfoisophthalic and mixtures thereof. Examples of suitable glycols include ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, 1,4-cyclohexanedimethanol, diethylene glycol, other polyethylene glycols and mixtures thereof. Such polyesters are well known in the art and may be produced by well-known techniques, e.g., those described in U.S. Pat. Nos. 2,465,319 and 2,901,466. Preferred continuous matrix polyesters are those having repeat units from terephthalic acid or naphthalene dicarboxylic acid and at least one glycol selected from ethylene glycol, 1,4-butanediol and 1,4-cyclohexanedimethanol. Poly(ethylene terephthalate), which may be modified by small amounts of other monomers, is especially preferred. Other suitable polyesters include liquid crystal copolyesters formed by the inclusion of suitable amount of a co-acid component such as stilbene dicarboxylic acid. Examples of such liquid crystal copolyesters are those disclosed in U.S. Pat. Nos. 4,420,607; 4,459,402; and 4,468,510.

[0057] Useful polyamides for base sheet include nylon 6, nylon 66, and mixtures thereof. Copolymers of polyamides are also suitable continuous phase polymers. An example of a useful polycarbonate is bisphenol-A polycarbonate. Cellulosic esters suitable for use as the continuous phase polymer of the composite sheets include cellulose nitrate, cellulose triacetate, cellulose diacetate, cellulose acetate propionate, cellulose acetate butyrate, and mixtures or copolymers thereof. Useful polyvinyl resins include polyvinyl chloride, poly(vinyl acetal), and mixtures thereof. Copolymers of vinyl resins can also be utilized.

[0058] Addenda is preferably added to the base sheet to improve the whiteness of these sheets. This would include any process which is known in the art including adding a white pigment, such as titanium dioxide, barium sulfate, clay, or calcium carbonate. This would also include adding fluorescing agents which absorb energy in the ultraviolet region and emit light largely in the blue region, or other additives which would improve the physical properties of the sheet or the manufacturability of the sheet.

[0059] The preferred thickness of the base sheet is less than 100 micrometers. The most preferred thickness of the base polymer sheet is between 20 and 80 micrometers. At a base thickness less than 15 micrometers it is difficult to provide required reflection properties for the base sheet. At thickness greater than 100 micrometers, little improvement in image optical properties such as image sharpness and lightness has been observed.

[0060] For a white, reflective photographic label, the preferred optical transmission of the base polymer sheet is less than 25%. It has been found that polymer sheets with optical transmission greater than 30% have density minimum areas of the print that appear dark. Also, a white label, one that has an optical transmission less than 25% conveys a perceived sense of quality and cleanness that is consistent with a high quality packaging label.

[0061] The coextrusion, quenching, orienting, and heat setting of the polymer base sheet may be effected by any process which is known in the art for producing oriented sheet, such as by a flat sheet process or a bubble or tubular process. The flat sheet process involves extruding or coextruding the blend through a slit die and rapidly quenching the extruded or coextruded web upon a chilled casting drum so that the polymer component(s) of the sheet are quenched below their solidification temperature. The quenched base sheet is then biaxially oriented by stretching in mutually perpendicular directions at a temperature above the glass transition temperature of the polymer(s). The sheet may be stretched in one direction and then in a second direction, or may be simultaneously stretched in both directions. After the sheet has been stretched, it is heat set by heating to a temperature sufficient to crystallize the polymers while restraining to some degree the sheet against retraction in both directions of stretching.

[0062] To adhere the transparent polymer sheet with the developed image layers to the base sheet of the invention a bonding layer is required. The bonding layer must provide excellent adhesion between the imaging layers and the base sheet for the useful life of the image. The preferred method of adhering the imaging layers and the base sheet is

by use of an adhesive. The adhesive preferably is coated or applied to the base sheet. The adhesive preferably is a pressure sensitive adhesive or heat activated adhesive. During the bonding process, the imaging layers is adhered to the base by use of a nip roller or a heated nip roll in the case of a heat activated adhesive

[0063] A preferred covering material suitable for a silver halide packaging label is detailed below. The oriented polyester with the integral oriented polyethylene skin layer is coated with light sensitive silver halide imaging layers, exposed, and processed. The post process image is then laminated with an acrylic pressure sensitive adhesive to a pre-formed, three layer biaxially oriented polypropylene base sheet. This photographic label structure is suitable for application to a PET beverage bottle using an adhesive applied to the exposed polypropylene layer to adhere the photographic label to the PET bottle.

| |
|---|
| Oriented polyester |
| Oriented polyethylene |
| Developed silver halide imaging layers |
| Acrylic pressure sensitive adhesive |
| Oriented polypropylene with optical brightener and TiO_2 |
| Oriented voided polypropylene |
| Oriented polypropylene |

[0064] Another preferred covering material suitable for a silver halide packaging label is detailed below. The oriented polypropylene with the integral oriented polyethylene skin layer is coated with light sensitive silver halide imaging layers, exposed and processed. The post process image is then laminated with an acrylic pressure sensitive adhesive to a preformed, integral three layer biaxially oriented polypropylene base sheet that contains a vacuum deposited aluminum layer. This label structure is suitable for a bag containing fried snack food where the bag is formed around a forming collar and filled with fried snack food. The aluminum layer is on the inside of the formed bag.

| |
|---|
| Oriented polyester |
| Oriented polyethylene with blue tint and a UV filter |
| Developed silver halide imaging layers |
| Acrylic pressure sensitive adhesive |
| Oriented polypropylene with optical brightener and TiO_2 |
| Oriented voided polypropylene |
| Oriented polyethylene |
| Vacuum deposited aluminum |

[0065] Disclosed below is a suitable flesh tone optimized light sensitive silver halide emulsion capable of accurately reproducing flesh tones. This invention is also directed to a silver halide packaging label capable of excellent performance when exposed by either an electronic printing method or a conventional optical printing method. An electronic printing method comprises subjecting a radiation sensitive silver halide emulsion layer of a recording element to actinic radiation of at least 10^{-4} ergs/cm² for up to 100 μ seconds duration in a pixel-by-pixel mode wherein the silver halide emulsion layer is comprised of silver halide grains as described above. A conventional optical printing method comprises subjecting a radiation sensitive silver halide emulsion layer of a recording element to actinic radiation of at least 10^{-4} ergs/cm² for 10^{-3} to 300 seconds in an imagewise mode wherein the silver halide emulsion layer is comprised of silver halide grains as described above.

[0066] This invention in a preferred embodiment utilizes a radiation-sensitive emulsion comprised of silver halide grains (a) containing greater than 50 mole percent chloride, based on silver, (b) having greater than 50 percent of their surface area provided by {100} crystal faces, and (c) having a central portion accounting for from 95 to 99 percent of

total silver and containing two dopants selected to satisfy each of the following class requirements: (i) a hexacoordination metal complex which satisfies the formula (I)



wherein n is zero, -1, -2, -3 or -4; M is a filled frontier orbital polyvalent metal ion, other than iridium; and L_6 represents bridging ligands which can be independently selected, provided that least four of the ligands are anionic ligands, and at least one of the ligands is a cyano ligand or a ligand more electronegative than a cyano ligand; and (ii) an iridium coordination complex containing a thiazole or substituted thiazole ligand.

[0067] This invention is directed towards a photographic label comprising a flexible substrate and at least one light sensitive silver halide emulsion layer comprising silver halide grains as described above. The photographic label may be color or black and white where silver is retained in the developed imaging layer to form density.

[0068] It has been discovered quite surprisingly that the combination of dopants (i) and (ii) provides greater reduction in reciprocity law failure than can be achieved with either dopant alone. Further, unexpectedly, the combination of dopants (i) and (ii) achieve reductions in reciprocity law failure beyond the simple additive sum achieved when employing either dopant class by itself. It has not been reported or suggested prior to this invention that the combination of dopants (i) and (ii) provides greater reduction in reciprocity law failure, particularly for high intensity and short duration exposures. The combination of dopants (i) and (ii) further unexpectedly achieves high intensity reciprocity with iridium at relatively low levels, and both high and low intensity reciprocity improvements even while using conventional gelatino-peptizer (e.g., other than low methionine gelatino-peptizer).

[0069] In a preferred practical application, the advantages of the invention can be transformed into increased throughput of digital substantially artifact-free color print images while exposing each pixel sequentially in synchronism with the digital data from an image processor.

[0070] In one embodiment, the present invention represents an improvement on the electronic printing method. Specifically, this invention in one embodiment is directed to an electronic printing method which comprises subjecting a radiation sensitive silver halide emulsion layer of a recording element to actinic radiation of at least 10^{-4} ergs/cm² for up to 100 μ seconds duration in a pixel-by-pixel mode. The present invention realizes an improvement in reciprocity failure by selection of the radiation sensitive silver halide emulsion layer. While certain embodiments of the invention are specifically directed towards electronic printing, use of the emulsions and elements of the invention is not limited to such specific embodiment, and it is specifically contemplated that the emulsions and elements of the invention are also well suited for conventional optical printing.

[0071] It has been unexpectedly discovered that significantly improved reciprocity performance can be obtained for silver halide grains (a) containing greater than 50 mole percent chloride, based on silver, and (b) having greater than 50 percent of their surface area provided by {100} crystal faces by employing a hexacoordination complex dopant of class (1) in combination with an iridium complex dopant comprising a thiazole or substituted thiazole ligand. The reciprocity improvement is obtained for silver halide grains employing conventional gelatino-peptizer, unlike the contrast improvement described for the combination of dopants set forth in U.S. Patents 5,783,373 and 5,783,378, which requires the use of low methionine gelatino-peptizers as discussed therein, and which states it is preferable to limit the concentration of any gelatino-peptizer with a methionine level of greater than 30 micromoles per gram to a concentration of less than 1 percent of the total peptizer employed. Accordingly, in specific embodiments of the invention, it is specifically contemplated to use significant levels (i.e., greater than 1 weight percent of total peptizer) of conventional gelatin (e.g., gelatin having at least 30 micromoles of methionine per gram) as a gelatino-peptizer for the silver halide grains of the emulsions of the invention. In preferred embodiments of the invention, gelatino-peptizer is employed which comprises at least 50 weight percent of gelatin containing at least 30 micromoles of methionine per gram, as it is frequently desirable to limit the level of oxidized low methionine gelatin which may be used for cost and certain performance reasons.

[0072] In a specific, preferred form of the invention it is contemplated to employ a class (i) hexacoordination complex dopant satisfying the formula: (I)



where

n is zero, -1, -2, -3 or -4;

M is a filled frontier orbital polyvalent metal ion, other than iridium, preferably Fe⁺², Ru⁺², Os⁺², Co⁺³, Rh⁺³, Pd⁺⁴ or Pt⁺⁴, more preferably an iron, ruthenium or osmium ion, and most preferably a ruthenium ion;

L_6 represents six bridging ligands which can be independently selected, provided that least four of the ligands are anionic ligands and at least one (preferably at least 3 and optimally at least 4) of the ligands is a cyano ligand or a ligand more electronegative than a cyano ligand. Any remaining ligands can be selected from among various other

bridging ligands, including aquo ligands, halide ligands (specifically, fluoride, chloride, bromide and iodide), cyanate ligands, thiocyanate ligands, selenocyanate ligands, tellurocyanate ligands, and azide ligands. Hexacoordinated transition metal complexes of class (i) which include six cyano ligands are specifically preferred.

5 **[0073]** Illustrations of specifically contemplated class (i) hexacoordination complexes for inclusion in the high chloride grains are provided by Olm et al U.S. Patent 5,503,970 and Daubendiek et al U.S. Patents 5,494,789 and 5,503,971, and Keevert et al U.S. Patent 4,945,035, as well as Murakami et al Japanese Patent Application Hei-2[1990]-249588, and *Research Disclosure* Item 36736. Useful neutral and anionic organic ligands for class (ii) dopant hexacoordination complexes are disclosed by Olm et al U.S. Patent 5,360,712 and Kuromoto et al U.S. Patent 10 5,462,849.

[0074] Class (i) dopant is preferably introduced into the high chloride grains after at least 50 (most preferably 75 and optimally 80) percent of the silver has been precipitated, but before precipitation of the central portion of the grains has been completed. Preferably class (i) dopant is introduced before 98 (most preferably 95 and optimally 90) percent of the silver has been precipitated. Stated in terms of the fully precipitated grain structure, class (i) dopant is preferably 15 present in an interior shell region that surrounds at least 50 (most preferably 75 and optimally 80) percent of the silver and, with the more centrally located silver, accounts the entire central portion (99 percent of the silver), most preferably accounts for 95 percent, and optimally accounts for 90 percent of the silver halides forming the high chloride grains. The class (i) dopant can be distributed throughout the interior shell region delimited above or can be added as one or more bands within the interior shell region.

20 **[0075]** Class (i) dopant can be employed in any conventional useful concentration. A preferred concentration range is from 10^{-8} to 10^{-3} mole per silver mole, most preferably from 10^{-6} to 5×10^{-4} mole per silver mole.

[0076] The following are specific illustrations of class (i) dopants:

- (i-1) $[\text{Fe}(\text{CN})_6]^{-4}$
- 25 (i-2) $[\text{Ru}(\text{CN})_6]^{-4}$
- (i-3) $[\text{Os}(\text{CN})_6]^{-4}$
- (i-4) $[\text{Rh}(\text{CN})_6]^{-3}$
- (i-5) $[\text{Co}(\text{CN})_6]^{-3}$
- (i-6) $[\text{Fe}(\text{pyrazine})(\text{CN})_5]^{-4}$
- 30 (i-7) $[\text{RuCl}(\text{CN})_5]^{-4}$
- (i-8) $[\text{OsBr}(\text{CN})_5]^{-4}$
- (i-9) $[\text{RhF}(\text{CN})_5]^{-3}$
- (i-10) $[\text{In}(\text{NCS})_6]^{-3}$
- (i-11) $[\text{FeCO}(\text{CN})_5]^{-3}$
- 35 (i-12) $[\text{RuF}_2(\text{CN})_4]^{-4}$
- (i-13) $[\text{OsCl}_2(\text{CN})_4]^{-4}$
- (i-14) $[\text{RhI}_2(\text{CN})_4]^{-3}$
- (i-15) $[\text{Ga}(\text{NCS})_6]^{-3}$
- (i-16) $[\text{Ru}(\text{CN})_5(\text{OCN})]^{-4}$
- 40 (i-17) $[\text{Ru}(\text{CN})_5(\text{N}_3)]^{-4}$
- (i-18) $[\text{Os}(\text{CN})_5(\text{SCN})]^{-4}$
- (i-19) $[\text{Rh}(\text{CN})_5(\text{SeCN})]^{-3}$
- (i-20) $[\text{Os}(\text{CN})\text{Cl}_5]^{-4}$
- (i-21) $[\text{Fe}(\text{CN})_3\text{Cl}_3]^{-3}$
- 45 (i-22) $[\text{Ru}(\text{CO})_2(\text{CN})_4]^{-1}$

[0077] When the class (i) dopants have a net negative charge, it is appreciated that they are associated with a counter ion when added to the reaction vessel during precipitation. The counter ion is of little importance, since it is ionically dissociated from the dopant in solution and is not incorporated within the grain. Common counter ions known to be fully compatible with silver chloride precipitation, such as ammonium and alkali metal ions, are contemplated. It is noted that the same comments apply to class (ii) dopants, otherwise described below.

[0078] The class (ii) dopant is an iridium coordination complex containing at least one thiazole or substituted thiazole ligand. Careful scientific investigations have revealed Group VIII hexahalo coordination complexes to create deep electron traps, as illustrated R. S. Eachus, R. E. Graves and M. T. Olm *J. Chem. Phys.*, Vol. 69, pp. 4580-7 (1978) and 55 *Physica Status Solidi A*, Vol. 57, 429-37 (1980) and R. S. Eachus and M. T. Olm *Annu. Rep. Prog. Chem. Sect. C. Phys. Chem.*, Vol. 83, 3, pp. 3-48 (1986). The class (ii) dopants employed in the practice of this invention are believed to create such deep electron traps. The thiazole ligands may be substituted with any photographically acceptable substituent which does not prevent incorporation of the dopant into the silver halide grain. Exemplary substituents include

lower alkyl (e.g., alkyl groups containing 1-4 carbon atoms), and specifically methyl. A specific example of a substituted thiazole ligand which may be used in accordance with the invention is 5-methylthiazole. The class (ii) dopant preferably is an iridium coordination complex having ligands each of which are more electropositive than a cyano ligand. In a specifically preferred form the remaining non-thiazole or non-substituted-thiazole ligands of the coordination complexes forming class (ii) dopants are halide ligands.

[0079] It is specifically contemplated to select class (ii) dopants from among the coordination complexes containing organic ligands disclosed by Olm et al U.S. Patents 5,360,712 and 5,457,021 and Kuromoto et al U.S. Patent 5,462,849.

[0080] In a preferred form it is contemplated to employ as a class (ii) dopant a hexacoordination complex satisfying the formula: (II)



wherein

n' is zero, -1, -2, -3 or -4; and

L_6 represents six bridging ligands which can be independently selected, provided that at least four of the ligands are anionic ligands, each of the ligands is more electropositive than a cyano ligand, and at least one of the ligands comprises a thiazole or substituted thiazole ligand. In a specifically preferred form at least four of the ligands are halide ligands, such as chloride or bromide ligands.

[0081] Class (ii) dopant is preferably introduced into the high chloride grains after at least 50 (most preferably 85 and optimally 90) percent of the silver has been precipitated, but before precipitation of the central portion of the grains has been completed. Preferably class (ii) dopant is introduced before 99 (most preferably 97 and optimally 95) percent of the silver has been precipitated. Stated in terms of the fully precipitated grain structure, class (ii) dopant is preferably present in an interior shell region that surrounds at least 50 (most preferably 85 and optimally 90) percent of the silver and, with the more centrally located silver, accounts the entire central portion (99 percent of the silver), most preferably accounts for 97 percent, and optimally accounts for 95 percent of the silver halide forming the high chloride grains. The class (ii) dopant can be distributed throughout the interior shell region delimited above or can be added as one or more bands within the interior shell region.

[0082] Class (ii) dopant can be employed in any conventional useful concentration. A preferred concentration range is from 10^{-9} to 10^{-4} mole per silver mole. Iridium is most preferably employed in a concentration range of from 10^{-8} to 10^{-5} mole per silver mole.

[0083] Specific illustrations of class (ii) dopants are the following:

- (ii-1) $[\text{IrCl}_5(\text{thiazole})]^{-2}$
- (ii-2) $[\text{IrCl}_4(\text{thiazole})_2]^{-1}$
- (ii-3) $[\text{IrBr}_5(\text{thiazole})]^{-2}$
- (ii-4) $[\text{IrBr}_4(\text{thiazole})_2]^{-1}$
- (ii-5) $[\text{IrCl}_5(5\text{-methylthiazole})]^{-2}$
- (ii-6) $[\text{IrCl}_4(5\text{-methylthiazole})_2]^{-1}$
- (ii-7) $[\text{IrBr}_5(5\text{-methylthiazole})]^{-2}$
- (ii-8) $[\text{IrBr}_4(5\text{-methylthiazole})_2]^{-1}$

[0084] In one preferred aspect of the invention in a layer using a magenta dye forming coupler, a class (ii) dopant in combination with an $\text{OsCl}_5(\text{NO})$ dopant has been found to produce a preferred result.

[0085] Emulsions demonstrating the advantages of the invention can be realized by modifying the precipitation of conventional high chloride silver halide grains having predominantly (>50%) {100} crystal faces by employing a combination of class (i) and (ii) dopants as described above.

[0086] The silver halide grains precipitated contain greater than 50 mole percent chloride, based on silver. Preferably the grains contain at least 70 mole percent chloride and, optimally at least 90 mole percent chloride, based on silver. Iodide can be present in the grains up to its solubility limit, which is in silver iodochloride grains, under typical conditions of precipitation, about 11 mole percent, based on silver. It is preferred for most photographic applications to limit iodide to less than 5 mole percent iodide, most preferably less than 2 mole percent iodide, based on silver.

[0087] Silver bromide and silver chloride are miscible in all proportions. Hence, any portion, up to 50 mole percent, of the total halide not accounted for chloride and iodide, can be bromide. For color reflection print (i.e., color paper) uses

bromide is typically limited to less than 10 mole percent based on silver and iodide is limited to less than 1 mole percent based on silver.

[0088] In a widely used form high chloride grains are precipitated to form cubic grains--that is, grains having {100} major faces and edges of equal length. In practice ripening effects usually round the edges and corners of the grains to some extent. However, except under extreme ripening conditions substantially more than 50 percent of total grain surface area is accounted for by {100} crystal faces.

[0089] High chloride tetradecahedral grains are a common variant of cubic grains. These grains contain 6 {100} crystal faces and 8 {111} crystal faces. Tetradecahedral grains are within the contemplation of this invention to the extent that greater than 50 percent of total surface area is accounted for by {100} crystal faces.

[0090] Although it is common practice to avoid or minimize the incorporation of iodide into high chloride grains employed in color paper, it has been recently observed that silver iodochloride grains with {100} crystal faces and, in some instances, one or more {111} faces offer exceptional levels of photographic speed. In these emulsions iodide is incorporated in overall concentrations of from 0.05 to 3.0 mole percent, based on silver, with the grains having a surface shell of greater than 50 Å that is substantially free of iodide and an interior shell having a maximum iodide concentration that surrounds a core accounting for at least 50 percent of total silver. Such grain structures are illustrated by Chen et al EPO 0 718 679.

[0091] In another improved form the high chloride grains can take the form of tabular grains having {100} major faces. Preferred high chloride {100} tabular grain emulsions are those in which the tabular grains account for at least 70 (most preferably at least 90) percent of total grain projected area. Preferred high chloride {100} tabular grain emulsions have average aspect ratios of at least 5 (most preferably at least >8). Tabular grains typically have thicknesses of less than 0.3 µm, preferably less than 0.2 µm, and optimally less than 0.07 µm. High chloride {100} tabular grain emulsions and their preparation are disclosed by Maskasky U.S. Patents 5,264,337 and 5,292,632; House et al U.S. Patent 5,320,938; Brust et al U.S. Patent 5,314,798; and Chang et al U.S. Patent 5,413,904.

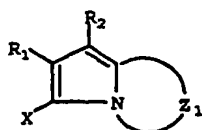
[0092] Once high chloride grains having predominantly {100} crystal faces have been precipitated with a combination of class (i) and class (ii) dopants described above, chemical and spectral sensitization, followed by the addition of conventional addenda to adapt the emulsion for the imaging application of choice can take any convenient conventional form. These conventional features are illustrated by *Research Disclosure*, Item 38957, cited above, particularly:

- III. Emulsion washing;
- IV. Chemical sensitization;
- V. Spectral sensitization and desensitization;
- VII. Antifoggants and stabilizers;
- VIII. Absorbing and scattering materials;
- IX. Coating and physical property modifying addenda; and
- X. Dye image formers and modifiers.

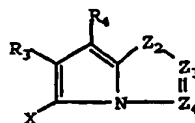
[0093] Some additional silver halide, typically less than 1 percent, based on total silver, can be introduced to facilitate chemical sensitization. It is also recognized that silver halide can be epitaxially deposited at selected sites on a host grain to increase its sensitivity. For example, high chloride {100} tabular grains with corner epitaxy are illustrated by Maskasky U.S. Patent 5,275,930. For the purpose of providing a clear demarcation, the term "silver halide grain" is herein employed to include the silver necessary to form the grain up to the point that the final {100} crystal faces of the grain are formed. Silver halide later deposited that does not overlie the {100} crystal faces previously formed accounting for at least 50 percent of the grain surface area is excluded in determining total silver forming the silver halide grains. Thus, the silver forming selected site epitaxy is not part of the silver halide grains while silver halide that deposits and provides the final {100} crystal faces of the grains is included in the total silver forming the grains, even when it differs significantly in composition from the previously precipitated silver halide.

[0094] Image dye-forming couplers may be included in the element such as couplers that form cyan dyes upon reaction with oxidized color developing agents which are described in such representative patents and publications as: U.S. Patent Nos. 2,367,531; 2,423,730; 2,474,293; 2,772,162; 2,895,826; 3,002,836; 3,034,892; 3,041,236; 4,883,746 and "Farbkuppler - Eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961). Preferably such couplers are phenols and naphthols that form cyan dyes on reaction with oxidized color developing agent. Also preferable are the cyan couplers described in, for instance, European Patent Application Nos. 491,197; 544,322; 556,700; 556,777; 565,096; 570,006; and 574,948.

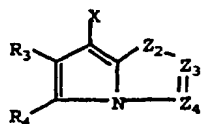
[0095] Typical cyan couplers are represented by the following formulas:



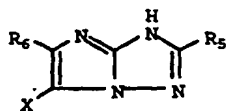
CYAN-1



CYAN-2



CYAN-3



CYAN-4

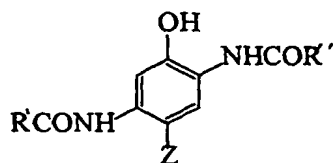
wherein R_1 , R_5 and R_8 each represents a hydrogen or a substituent; R_2 represents a substituent; R_3 , R_4 and R_7 each represents an electron attractive group having a Hammett's substituent constant σ_{para} of 0.2 or more and the sum of the σ_{para} values of R_3 and R_4 is 0.65 or more; R_6 represents an electron attractive group having a Hammett's substituent constant σ_{para} of 0.35 or more; X represents a hydrogen or a coupling-off group; Z_1 represents nonmetallic atoms necessary for forming a nitrogen-containing, six-membered, heterocyclic ring which has at least one dissociative group; Z_2 represents $-C(R_7)=$ and $-N=$; and Z_3 and Z_4 each represent $-C(R_8)=$ and $-N=$.

[0096] For purposes of this invention, an "NB coupler" is a dye-forming coupler which is capable of coupling with the developer 4-amino-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl) aniline sesquisulfate hydrate to form a dye for which the left bandwidth (LBW) of its absorption spectra upon "spin coating" of a 3% w/v solution of the dye in di-n-butyl sebacate solvent is at least 5 nm. less than the LBW for a 3% w/v solution of the same dye in acetonitrile. The LBW of the spectral curve for a dye is the distance between the left side of the spectral curve and the wavelength of maximum absorption measured at a density of half the maximum.

[0097] The "spin coating" sample is prepared by first preparing a solution of the dye in di-n-butyl sebacate solvent (3% w/v). If the dye is insoluble, dissolution is achieved by the addition of some methylene chloride. The solution is filtered and 0.1-0.2ml is applied to a clear polyethylene terephthalate support (approximately 4cm x 4cm) and spun at 4,000RPM using the Spin Coating equipment, Model No. EC101, available from Headway Research Inc., Garland TX. The transmission spectra of the so prepared dye samples are then recorded.

[0098] Preferred "NB couplers" form a dye which, in n-butyl sebacate, has a LBW of the absorption spectra upon "spin coating" which is at least 15 nm, preferably at least 25 nm, less than that of the same dye in a 3% solution (w/v) in acetonitrile.

[0099] In a preferred embodiment the cyan dye-forming "NB coupler" useful in the invention has the formula (IA)



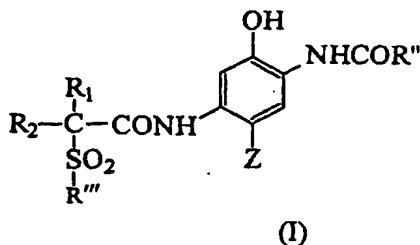
(IA)

wherein

R' and R'' are substituents selected such that the coupler is a "NB coupler", as herein defined; and Z is a hydrogen atom or a group which can be split off by the reaction of the coupler with an oxidized color developing agent.

[0100] The coupler of formula (IA) is a 2,5-diamido phenolic cyan coupler wherein the substituents R' and R'' are preferably independently selected from unsubstituted or substituted alkyl, aryl, amino, alkoxy and heterocyclyl groups.

[0101] In a further preferred embodiment, the "NB coupler" has the formula (I):



wherein

- 15 R^* and R''' are independently selected from unsubstituted or substituted alkyl, aryl, amino, alkoxy and heterocyclyl groups and Z is as hereinbefore defined;
 R_1 and R_2 are independently hydrogen or an unsubstituted or substituted alkyl group; and
 Typically, R'' is an alkyl, amino or aryl group, suitably a phenyl group. R''' is desirably an alkyl or aryl group or a 5-
 20 10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring group is unsubstituted or substituted.

[0102] In the preferred embodiment the coupler of formula (I) is a 2,5-diamido phenol in which the 5-amido moiety is an amide of a carboxylic acid which is substituted in the alpha position by a particular sulfone ($-SO_2$) group, such as, for example, described in U.S. Patent No. 5,686,235. The sulfone moiety is an unsubstituted or substituted alkylsulfone or a heterocyclyl sulfone or it is an arylsulfone, which is preferably substituted, in particular in the meta and/or para position.

[0103] Couplers having these structures of formulae (I) or (IA) comprise cyan dye-forming "NB couplers" which form image dyes having very sharp-cutting dye hues on the short wavelength side of the absorption curves with absorption maxima (λ_{max}) which are shifted hypsochromically and are generally in the range of 620-645 nm, which is ideally suited for producing excellent color reproduction and high color saturation in color photographic packaging labels.

[0104] Referring to formula (I), R_1 and R_2 are independently hydrogen or an unsubstituted or substituted alkyl group, preferably having from 1 to 24 carbon atoms and in particular 1 to 10 carbon atoms, suitably a methyl, ethyl, n-propyl, isopropyl, butyl or decyl group or an alkyl group substituted with one or more fluoro, chloro or bromo atoms, such as a trifluoromethyl group. Suitably, at least one of R_1 and R_2 is a hydrogen atom and if only one of R_1 and R_2 is a hydrogen atom then the other is preferably an alkyl group having 1 to 4 carbon atoms, more preferably one to three carbon atoms and desirably two carbon atoms.

[0105] As used herein and throughout the specification unless where specifically stated otherwise, the term "alkyl" refers to an unsaturated or saturated straight or branched chain alkyl group, including alkenyl, and includes aralkyl and cyclic alkyl groups, including cycloalkenyl, having 3-8 carbon atoms and the term "aryl" includes specifically fused aryl.

40 [0106] In formula (I), R^* is suitably an unsubstituted or substituted amino, alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted, but is more suitably an unsubstituted or substituted phenyl group.

[0107] Examples of suitable substituent groups for this aryl or heterocyclic ring include cyano, chloro, fluoro, bromo, iodo, alkyl- or aryl-carbonyl, alkyl- or aryl-oxycarbonyl, carbonamido, alkyl- or aryl-carbonamido, alkyl- or aryl-sulfonyl, alkyl- or aryl-sulfonyloxy, alkyl- or aryl-oxysulfonyl, alkyl- or aryl-sulfoxide, alkyl- or aryl-sulfamoyl, alkyl- or aryl-sulfonamido, aryl, alkyl, alkoxy, aryloxy, nitro, alkyl- or aryl-ureido and alkyl- or aryl-carbamoyl groups, any of which may be further substituted. Preferred groups are halogen, cyano, alkoxycarbonyl, alkylsulfamoyl, alkyl-sulfonamido, alkylsulfonyl, carbamoyl, alkylcarbamoyl or alkylcarbonamido. Suitably, R^* is a 4-chlorophenyl, 3,4-dichlorophenyl, 3,4-difluorophenyl, 4-cyanophenyl, 3-chloro-4-cyanophenyl, pentafluorophenyl, or a 3- or 4-sulfonamidophenyl group.

50 [0108] In formula (I), when R''' is alkyl it may be unsubstituted or substituted with a substituent such as halogen or alkoxy. When R''' is aryl or a heterocycle, it may be substituted. Desirably it is not substituted in the position alpha to the sulfonyl group.

[0109] In formula (I), when R''' is a phenyl group, it may be substituted in the meta and/or para positions with one to three substituents independently selected from the group consisting of halogen, and unsubstituted or substituted alkyl, alkoxy, aryloxy, acyloxy, acylamino, alkyl- or aryl-sulfonyloxy, alkyl- or aryl-sulfamoyl, alkyl- or aryl-sulfamoylamino, alkyl- or aryl-sulfonamido, alkyl- or aryl-ureido, alkyl- or aryl-oxycarbonyl, alkyl- or aryl-oxy-carbonylamino and alkyl- or aryl-carbamoyl groups.

[0110] In particular each substituent may be an alkyl group such as methyl, t-butyl, heptyl, dodecyl, pentadecyl,

octadecyl or 1,1,2,2-tetramethylpropyl; an alkoxy group such as methoxy, t-butoxy, octyloxy, dodecyloxy, tetradecyloxy, hexadecyloxy or octadecyloxy; an aryloxy group such as phenoxy, 4-t-butylphenoxy or 4-dodecyl-phenoxy; an alkyl- or aryl-acyloxy group such as acetoxy or dodecanoyloxy; an alkyl- or aryl-acylamino group such as acetamido, hexadecanamido or benzamido; an alkyl- or aryl-sulfonyloxy group such as methyl-sulfonyloxy, dodecylsulfonyloxy or 4-methyl-phenyl-sulfonyloxy; an alkyl- or aryl-sulfamoyl-group such as N-butylsulfamoyl or N-4-t-butylphenylsulfamoyl; an alkyl- or aryl-sulfamoylamino group such as N-butylsulfamoylamino or N-4-t-butylphenylsulfamoyl-amino; an alkyl- or aryl-sulfonamido group such as methane-sulfonamido, hexadecanesulfonamido or 4-chlorophenyl-sulfonamido; an alkyl- or aryl-ureido group such as methylureido or phenylureido; an alkoxy- or aryloxy-carbonyl such as methoxycarbonyl or phenoxy-carbonyl; an alkoxy- or aryloxy-carbonylamino group such as methoxycarbonylamino or phenoxy-carbonylamino; an alkyl- or aryl-carbamoyl group such as N-butylcarbamoyl or N-methyl-N-dodecylcarbamoyl; or a perfluoroalkyl group such as trifluoromethyl or heptafluoropropyl.

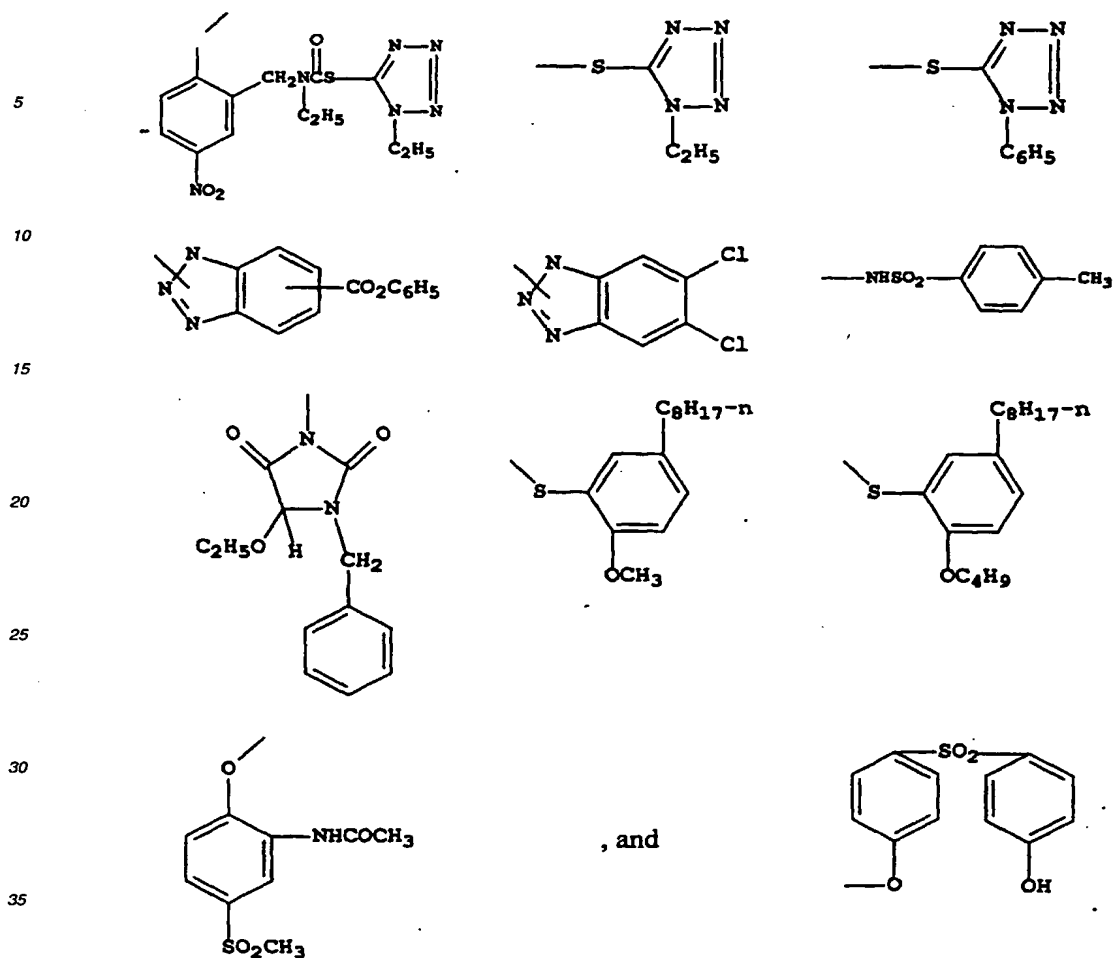
[0111] Suitably the above substituent groups have 1 to 30 carbon atoms, more preferably 8 to 20 aliphatic carbon atoms. A desirable substituent is an alkyl group of 12 to 18 aliphatic carbon atoms such as dodecyl, pentadecyl or octadecyl or an alkoxy group with 8 to 18 aliphatic carbon atoms such as dodecyloxy and hexadecyloxy or a halogen such as a meta or para chloro group, carboxy or sulfonamido. Any such groups may contain interrupting heteroatoms such as oxygen to form e.g. polyalkylene oxides.

[0112] In formula (I) or (IA) Z is a hydrogen atom or a group which can be split off by the reaction of the coupler with an oxidized color developing agent, known in the photographic art as a 'coupling-off group' and may preferably be hydrogen, chloro, fluoro, substituted aryloxy or mercaptotetrazole, more preferably hydrogen or chloro.

[0113] The presence or absence of such groups determines the chemical equivalency of the coupler, i.e., whether it is a 2-equivalent or 4-equivalent coupler, and its particular identity can modify the reactivity of the coupler. Such groups can advantageously affect the layer in which the coupler is coated, or other layers in the photographic recording material, by performing, after release from the coupler, functions such as dye formation, dye hue adjustment, development acceleration or inhibition, bleach acceleration or inhibition, electron transfer facilitation, color correction, and the like.

[0114] Representative classes of such coupling-off groups include, for example, halogen, alkoxy, aryloxy, heterocyclyloxy, sulfonyloxy, acyloxy, acyl, heterocyclylsulfonamido, heterocyclylthio, benzothiazolyl, phosphonyloxy, alkylthio, arylthio, and arylazo. These coupling-off groups are described in the art, for example, in U.S. Patent Nos. 2,455,169; 3,227,551; 3,432,521; 3,467,563; 3,617,291; 3,880,661; 4,052,212; and 4,134,766; and in U.K. Patent Nos. and published applications 1,466,728; 1,531,927; 1,533,039; 2,066,755A; and 2,017,704A. Halogen, alkoxy and aryloxy groups are most suitable.

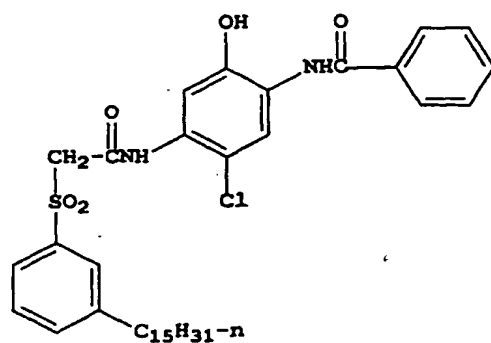
[0115] Examples of specific coupling-off groups are -Cl, -F, -Br, -SCN, -OCH₃, -OC₆H₅, -OCH₂C(=O)NHCH₂CH₂OH, -OCH₂C(O)NHCH₂CH₂OCH₃, -OCH₂C(O)NHCH₂CH₂OC(=O)OCH₃, -P(=O)(OC₂H₅)₂, -SCH₂CH₂COOH,



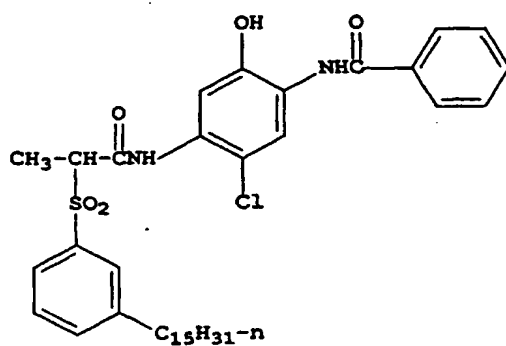
[0116] Typically, the coupling-off group is a chlorine atom, hydrogen atom or p-methoxyphenoxy group.

[0117] It is essential that the substituent groups be selected so as to adequately ballast the coupler and the resulting dye in the organic solvent in which the coupler is dispersed. The ballasting may be accomplished by providing hydrophobic substituent groups in one or more of the substituent groups. Generally a ballast group is an organic radical of such size and configuration as to confer on the coupler molecule sufficient bulk and aqueous insolubility as to render the coupler substantially nondiffusible from the layer in which it is coated in a photographic element. Thus the combination of substituent are suitably chosen to meet these criteria. To be effective, the ballast will usually contain at least 8 carbon atoms and typically contains 10 to 30 carbon atoms. Suitable ballasting may also be accomplished by providing a plurality of groups which in combination meet these criteria. In the preferred embodiments of the invention R_1 in formula (I) is a small alkyl group or hydrogen. Therefore, in these embodiments the ballast would be primarily located as part of the other groups. Furthermore, even if the coupling-off group Z contains a ballast it is often necessary to ballast the other substituents as well, since Z is eliminated from the molecule upon coupling; thus, the ballast is most advantageously provided as part of groups other than Z.

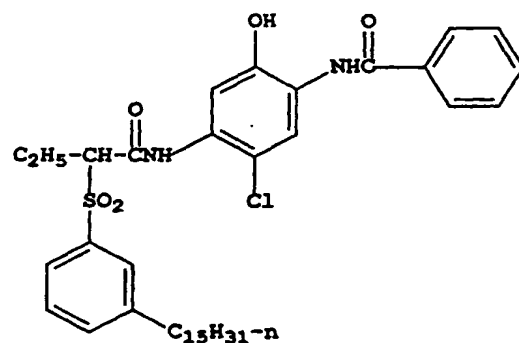
[0118] The following examples further illustrate preferred coupler of the invention. It is not to be construed that the present invention is limited to these examples.



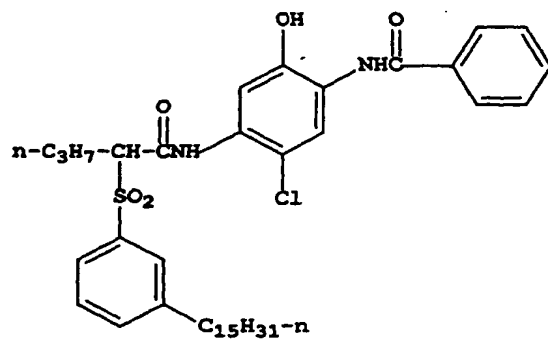
IC-1



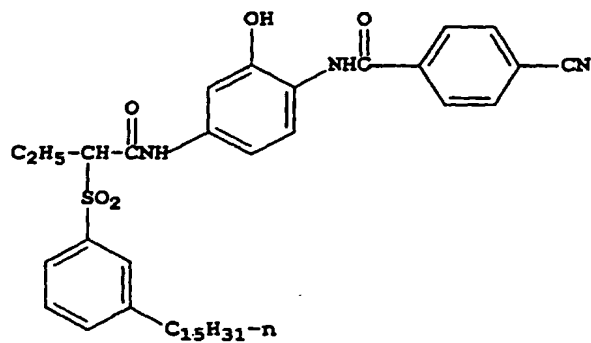
IC-2



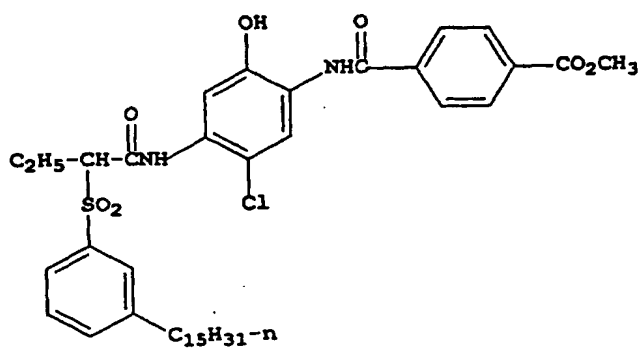
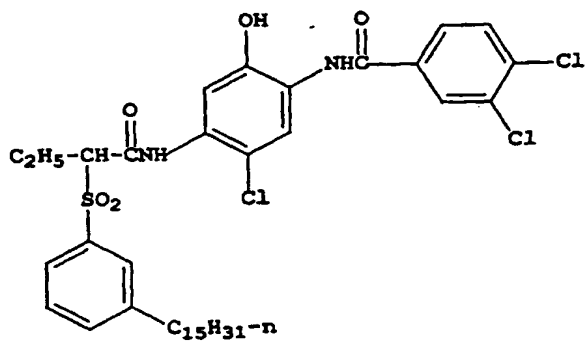
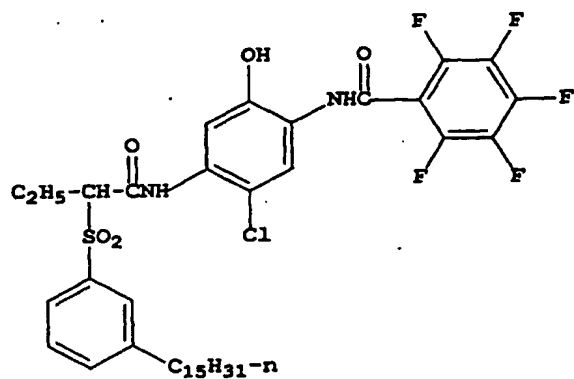
IC-3

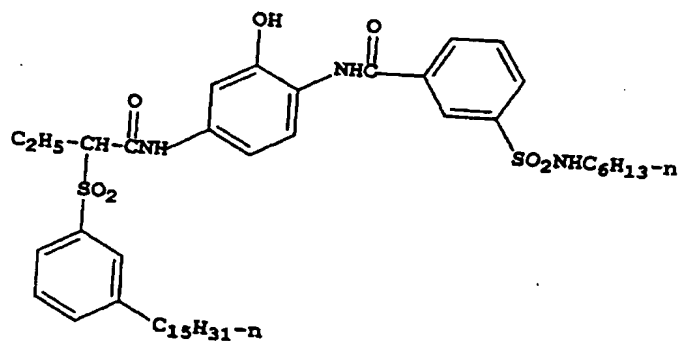


IC-4

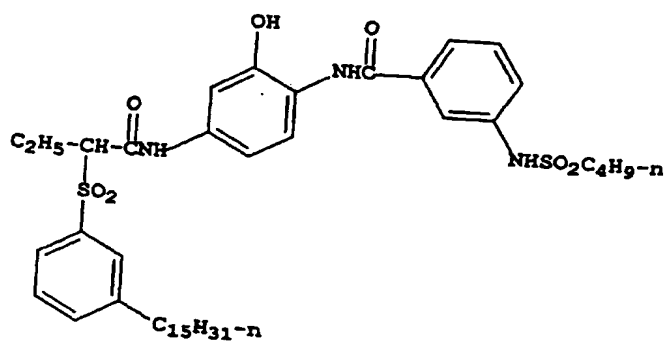


IC-5

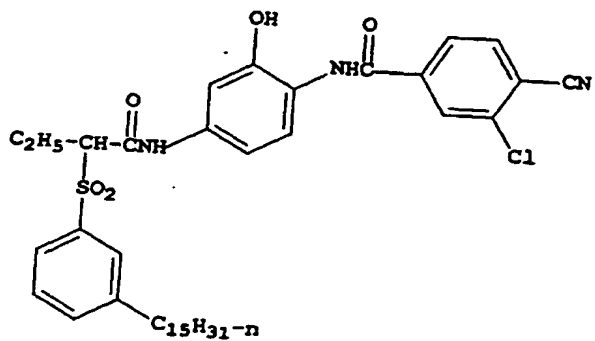




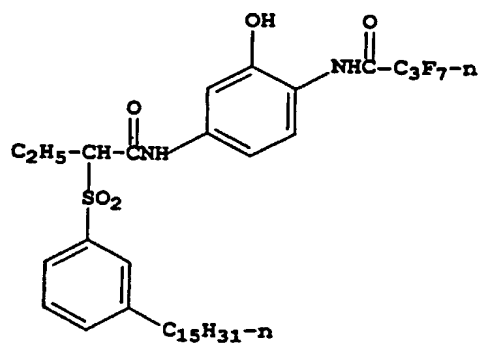
IC-9



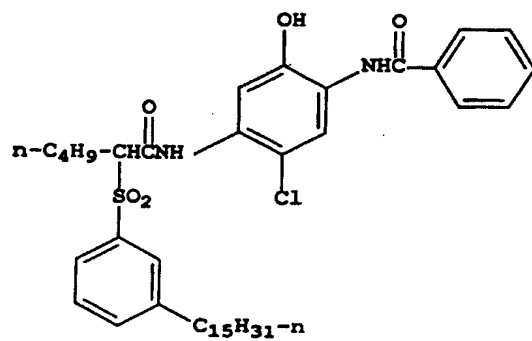
IC-10



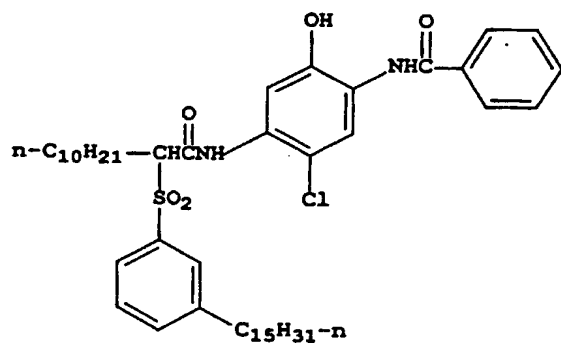
IC-11



IC-12



IC-13

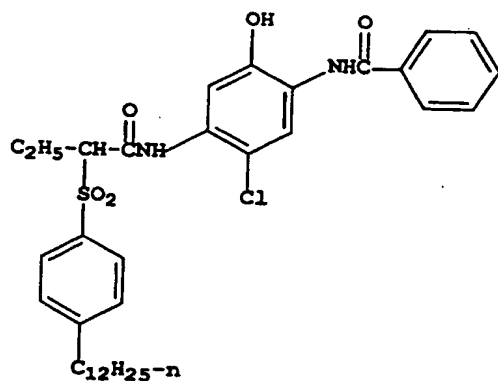


IC-14

5

10

15



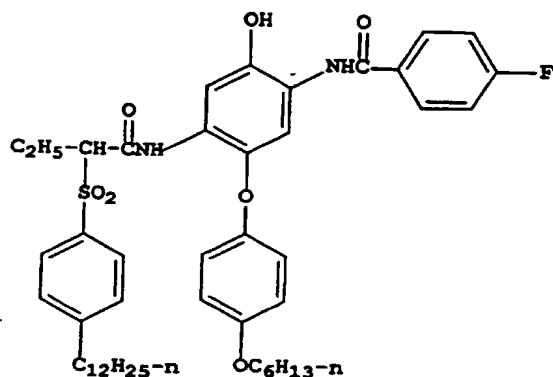
IC-15

20

25

30

35



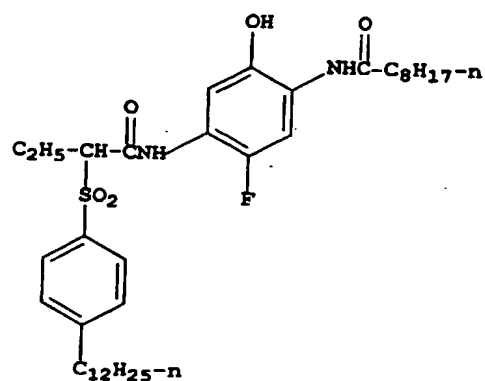
IC-16

40

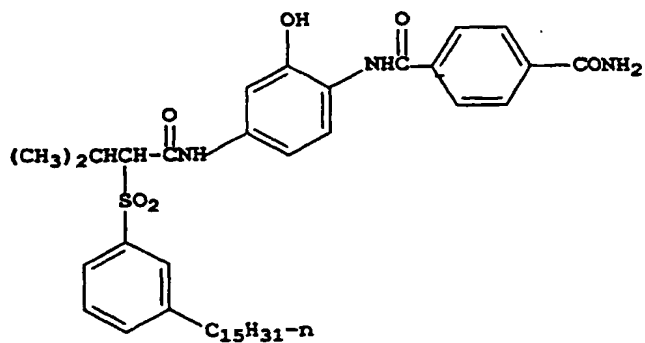
45

50

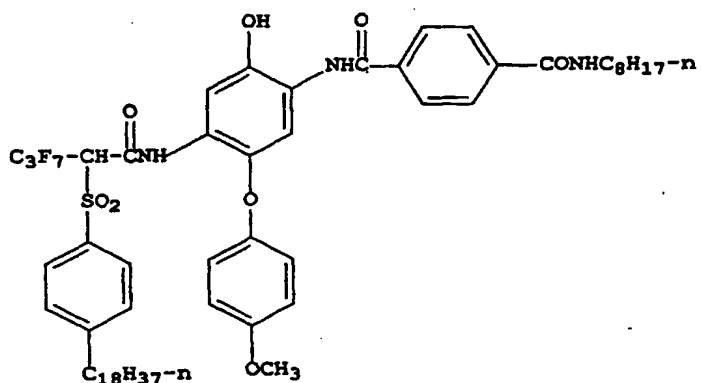
55



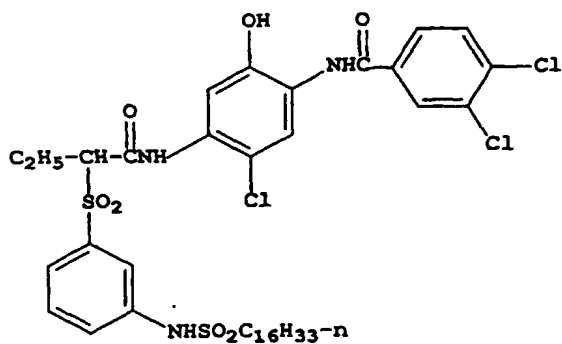
IC-17



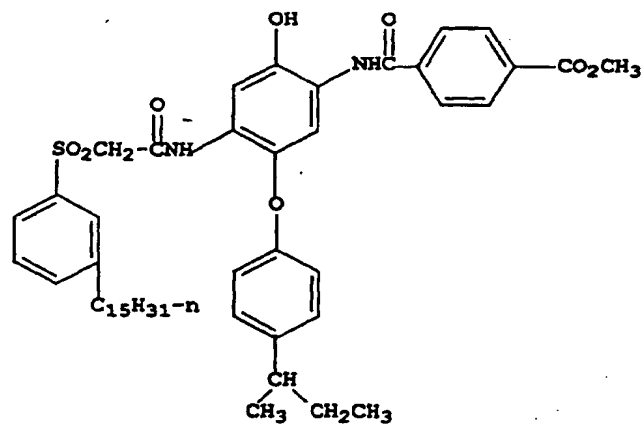
IC-18



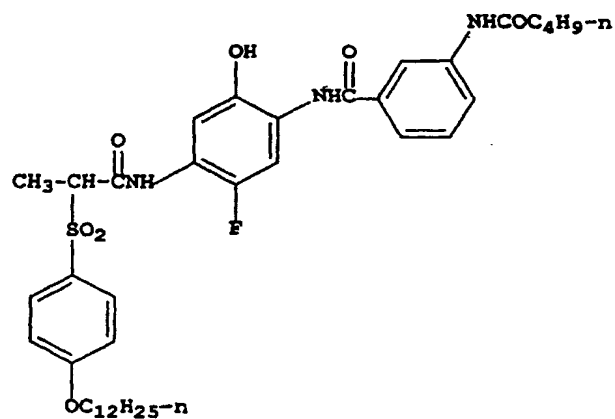
IC-19



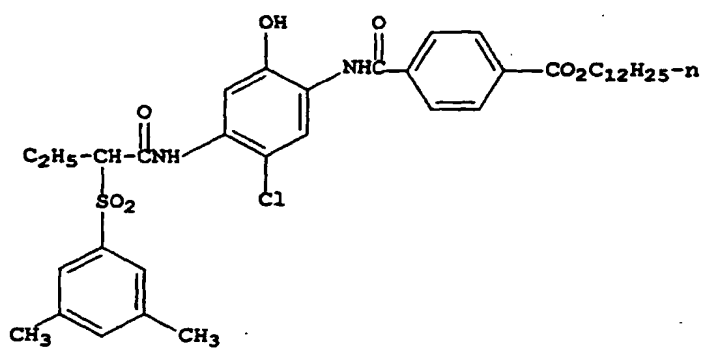
IC-20



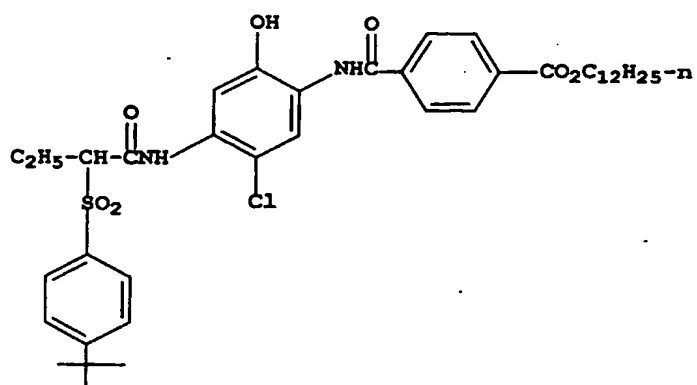
IC-21



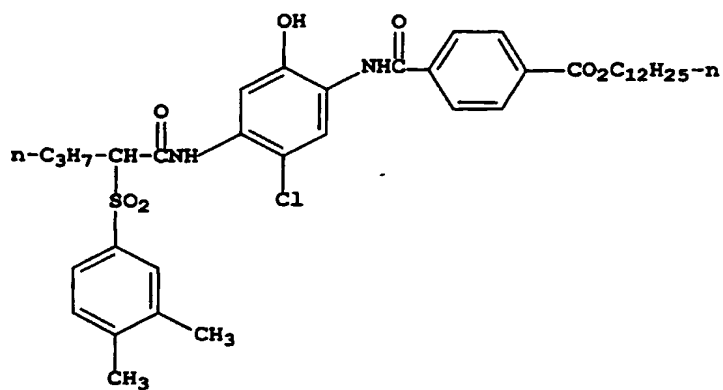
IC-22



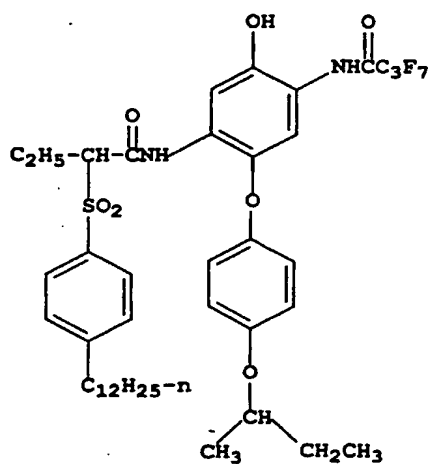
IC-23



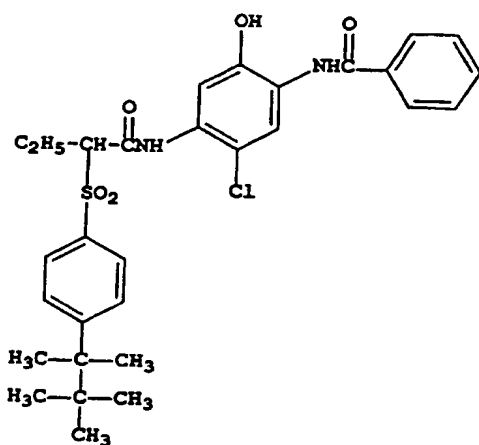
IC-24



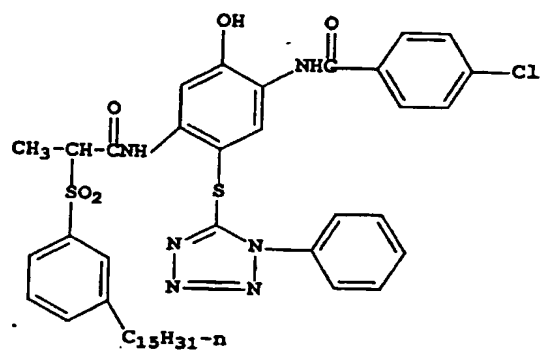
IC-25



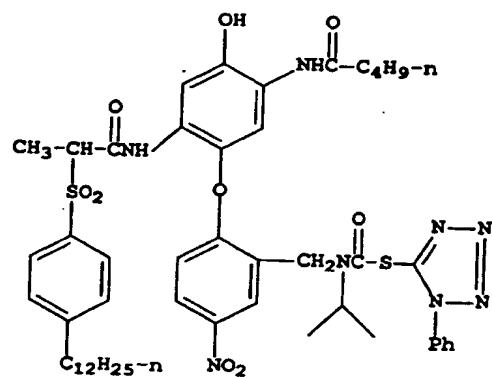
IC-26



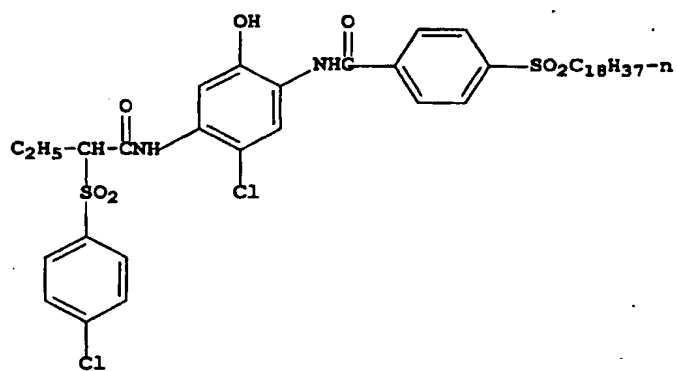
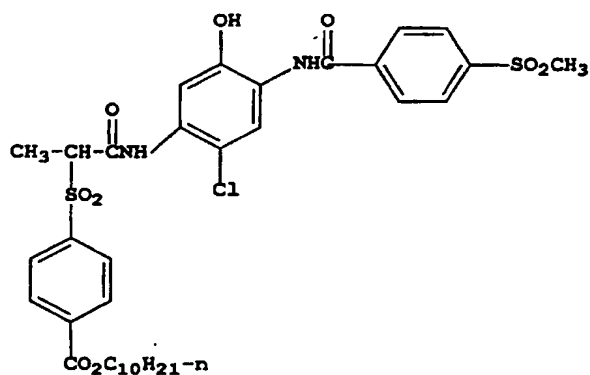
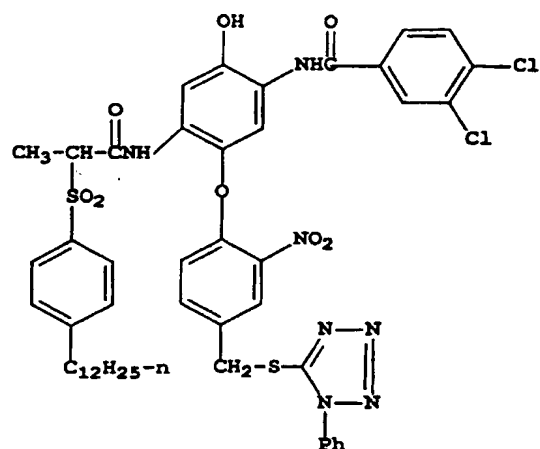
IC-27

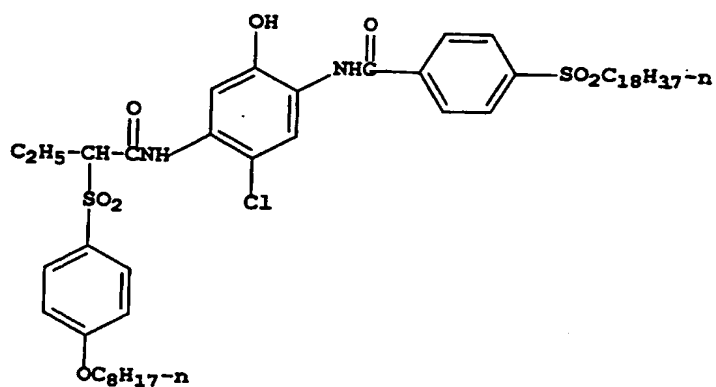


IC-28

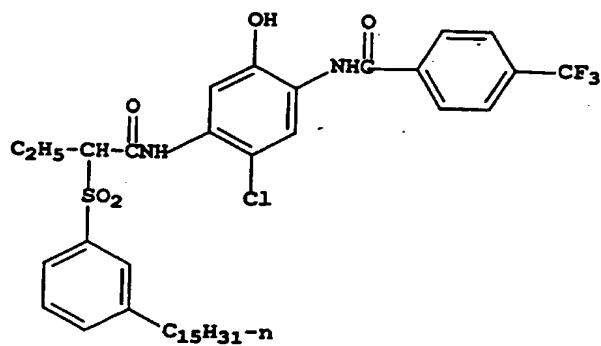


IC-29

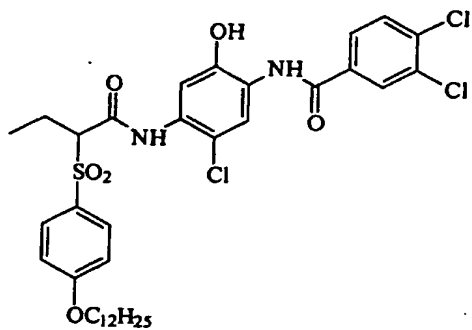




IC-33



IC-34



IC-35

5

10

15

20

25

30

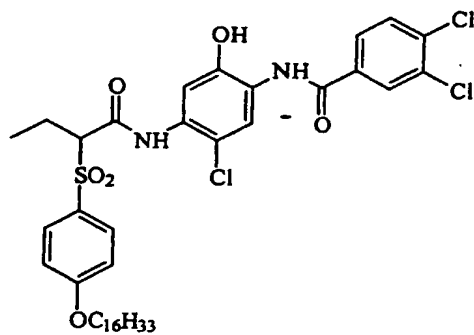
35

40

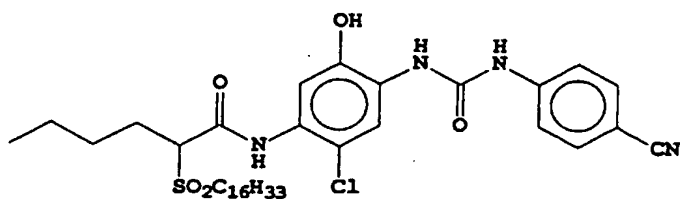
45

50

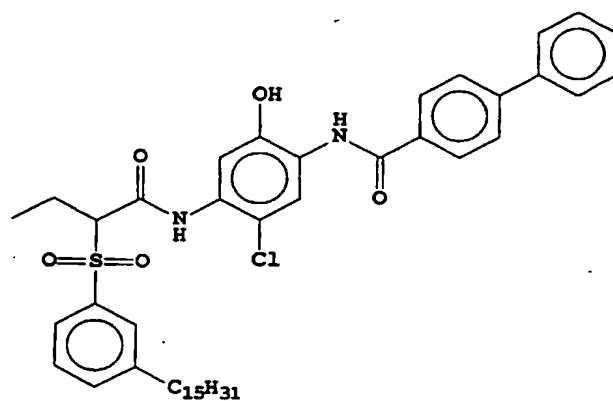
55



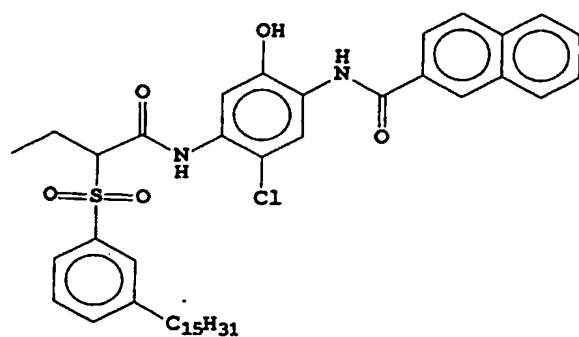
IC-36



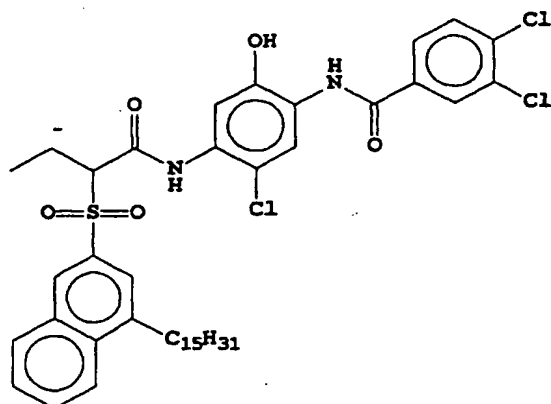
IC-37



IC-38



IC-39

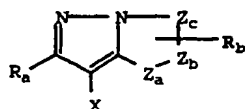


IC-40

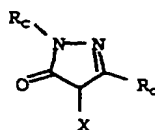
[0119] Preferred couplers are IC-3, IC-7, IC-35, and IC-36 because of their suitably narrow left bandwidths.

[0120] Couplers that form magenta dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,311,082, 2,343,703, 2,369,489, 2,600,788, 2,908,573, 3,062,653, 3,152,896, 3,519,429, 3,758,309, and "Farbkuppler-eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 126-156 (1961). Preferably such couplers are pyrazolones, pyrazolotriazoles, or pyrazolobenzimidazoles that form magenta dyes upon reaction with oxidized color developing agents. Especially preferred couplers are 1H-pyrazolo [5,1-c]-1,2,4-triazole and 1H-pyrazolo [1,5-b]-1,2,4-triazole. Examples of 1H-pyrazolo [5,1-c]-1,2,4-triazole couplers are described in U.K. Patent Nos. 1,247,493; 1,252,418; 1,398,979; U.S. Patent Nos. 4,443,536; 4,514,490; 4,540,654; 4,590,153; 4,665,015; 4,822,730; 4,945,034; 5,017,465; and 5,023,170. Examples of 1H-pyrazolo [1,5-b]-1,2,4-triazoles can be found in European Patent applications 176,804; 177,765; U.S. Patent Nos. 4,659,652; 5,066,575; and 5,250,400.

[0121] Typical pyrazoloazole and pyrazolone couplers are represented by the following formulas:



MAGENTA-1



MAGENTA-2

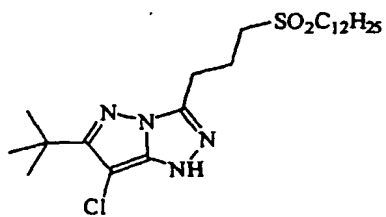
wherein R_a and R_b independently represent H or a substituent; R_c is a substituent (preferably an aryl group); R_d is a substituent (preferably an anilino, carbonamido, ureido, carbamoyl, alkoxy, aryloxy, carbonyl, alkoxy, carbonyl, or *N*-heterocyclic group); X is hydrogen or a coupling-off group; and Z_a , Z_b , and Z_c are independently a substituted methine group, $=N-$, $=C-$, or $-NH-$, provided that one of either the Z_a-Z_b bond or the Z_b-Z_c bond is a double bond and the other is a single bond, and when the Z_b-Z_c bond is a carbon-carbon double bond, it may form part of an aromatic ring, and at least one of Z_a , Z_b , and Z_c represents a methine group connected to the group R_b .

[0122] Specific examples of such couplers are:

M-1

5

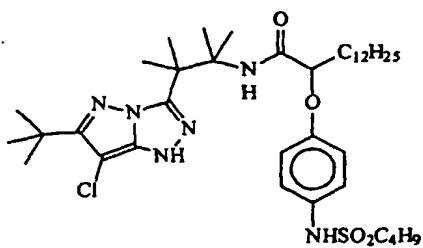
10



M-2

15

20



25

M-3

30

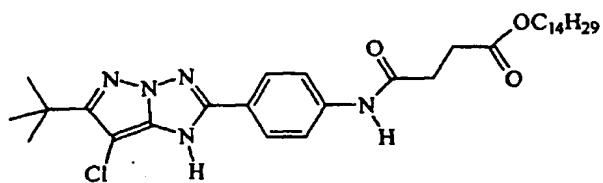
35

40

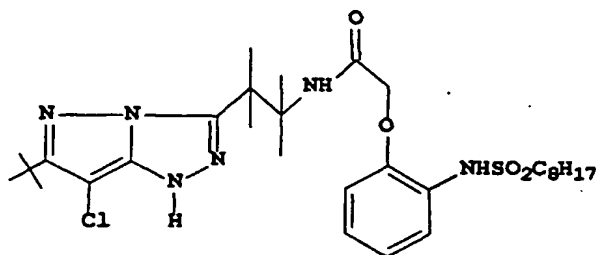
45

50

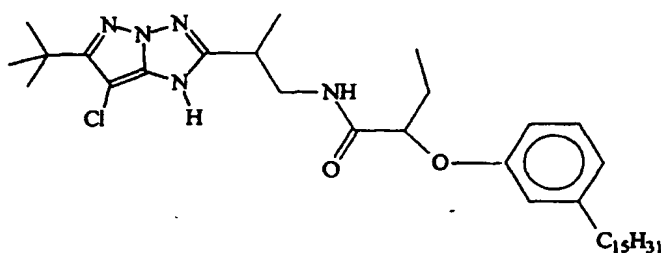
55



M-4

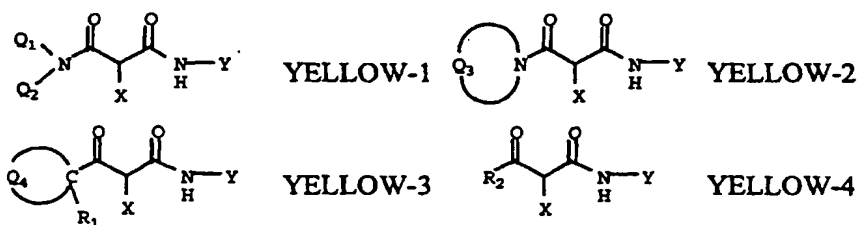


M-5



[0123] Couplers that form yellow dyes upon reaction with oxidized color developing agent are described in such representative patents and publications as: U.S. Patent Nos. 2,298,443; 2,407,210; 2,875,057; 3,048,194; 3,265,506; 3,447,928; 3,960,570; 4,022,620; 4,443,536; 4,910,126; and 5,340,703 and "Farbkuppler-eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961). Such couplers are typically open chain ketomethylene compounds. Also preferred are yellow couplers such as described in, for example, European Patent Application Nos. 482,552; 510,535; 524,540; 543,367; and U.S. Patent No. 5,238,803. For improved color reproduction, couplers which give yellow dyes that cut off sharply on the long wavelength side are particularly preferred (for example, see U.S. Patent No. 5,360,713).

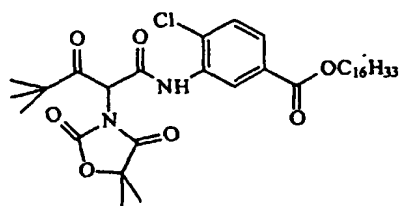
[0124] Typical preferred yellow couplers are represented by the following formulas:



wherein R_1 , R_2 , Q_1 and Q_2 each represents a substituent; X is hydrogen or a coupling-off group; Y represents an aryl group or a heterocyclic group; Q_3 represents an organic residue required to form a nitrogen-containing heterocyclic group together with the $>N-$; and Q_4 represents nonmetallic atoms necessary to form a 3- to 5-membered hydrocarbon ring or a 3- to 5-membered heterocyclic ring which contains at least one hetero atom selected from N, O, S, and P in the ring. Particularly preferred is when Q_1 and Q_2 each represents an alkyl group, an aryl group, or a heterocyclic group, and R_2 represents an aryl or tertiary alkyl group.

[0125] Preferred yellow couplers can be of the following general structures

Y-1

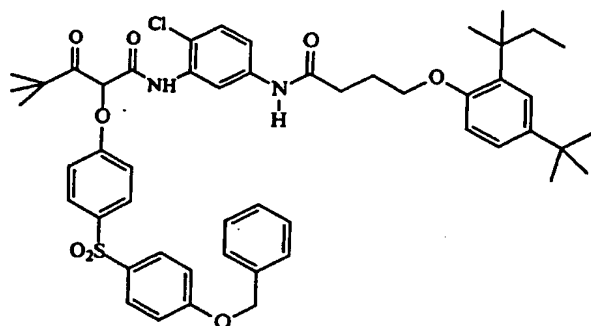


Y-2

5

10

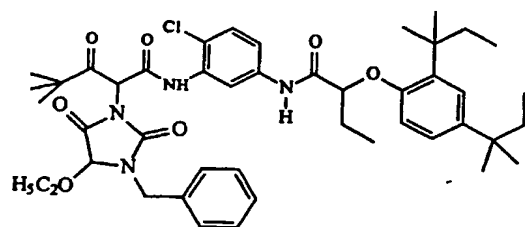
15



Y-3

20

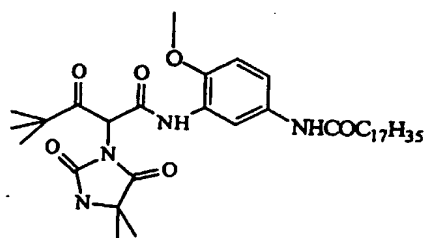
25



Y-4

30

35

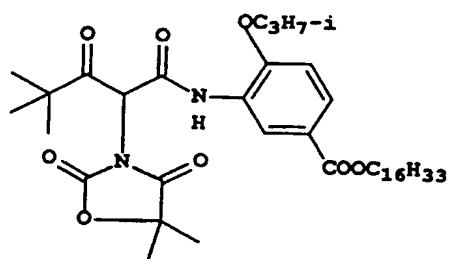


Y-5

40

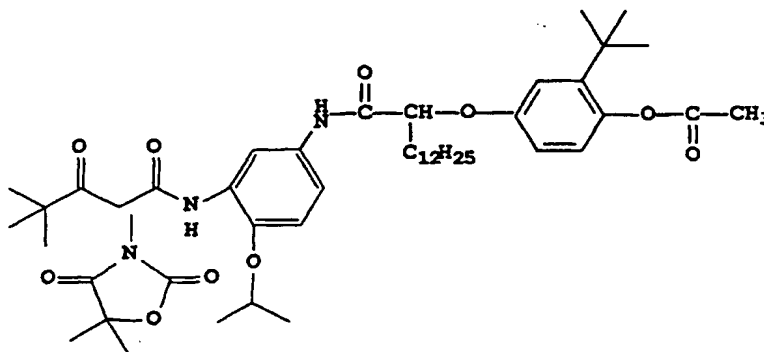
45

50



55

Y-6



[0126] Unless otherwise specifically stated, substituent groups which may be substituted on molecules herein include any groups, whether substituted or unsubstituted, which do not destroy properties necessary for photographic utility. When the term "group" is applied to the identification of a substituent containing a substitutable hydrogen, it is intended to encompass not only the substituent's unsubstituted form, but also its form further substituted with any group or groups as herein mentioned. Suitably, the group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous, or sulfur. The substituent may be, for example, halogen, such as chlorine, bromine or fluorine; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-*t*-pentylphenoxy) propyl, and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-*t*-pentylphenoxy)ethoxy, and 2-dodecyloxyethoxy; aryl such as phenyl, 4-*t*-butylphenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or betanaphthyl, and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-*t*-pentylphenoxy)acetamido, alpha-(2,4-di-*t*-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)-hexanamido, alpha-(4-hydroxy-3-*t*-butylphenoxy)-tetradecanamido, 2-oxo-pyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolidin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl, and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxycarbonylamino, hexadecyloxycarbonylamino, 2,4-di-*t*-butylphenoxycarbonylamino, phenylcarbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecyl-phenylcarbonylamino, *p*-toluylcarbonylamino, N-methylureido, N-methylureido, N-methyl-N-dodecylureido, N-hexadecylureido, N,N-dioctadecylureido, N,N-dioctyl-N'-ethylureido, N-phenylureido, N,N-diphenylureido, N-phenyl-N-*p*-toluylureido, N-(*m*-hexadecylphenyl)ureido, N,N-(2,5-di-*t*-pentylphenyl)-N'-ethylureido, and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-toluylsulfonamido, *p*-dodecylbenzenesulfonamido, N-methyltetradecylsulfonamido, N,N-dipropyl-sulfamoylamino, and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl; N-[3-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]sulfamoyl, N-methyl-N-tetradecylsulfamoyl, and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]carbamoyl, N-methyl-N-tetradecylcarbamoyl, and N,N-dioctylcarbamoyl; acyl, such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl, phenoxycarbonyl, *p*-dodecyloxyphenoxycarbonyl, methoxycarbonyl, butoxycarbonyl, tetradecyloxy carbonyl, ethoxycarbonyl, benzyloxycarbonyl, 3-pentadecyloxy carbonyl, and dodecyloxy carbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxysulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl, and *p*-toluylsulfonyl; sulfonyloxy, such as dodecylsulfonyloxy, and hexadecylsulfonyloxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecylsulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl, and *p*-toluylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-*t*-octylphenylthio, and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamidobenzoyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy, and cyclohexylcarbamoyloxy; amino, such as phenylanilino, 2-chloroanilino, diethylamino, dodecylamino; imino, such as 1 (N-phenylimido)ethyl, N-succinimido or 3-benzylhydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3- to 7-membered heterocyclic ring composed of car-

bon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen and sulfur, such as 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; and silyloxy, such as trimethylsilyloxy.

[0127] If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking groups, releasing or releasable groups, etc. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

[0128] Representative substituents on ballast groups include alkyl, aryl, alkoxy, aryloxy, alkylthio, hydroxy, halogen, alkoxycarbonyl, aryloxycarbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkylsulfonyl, arylsulfonyl, sulfonamido, and sulfamoyl groups wherein the substituents typically contain 1 to 42 carbon atoms. Such substituents can also be further substituted.

[0129] Silver halide imaging layers substantially free of stabilizers are preferred. Silver halide stabilizers are typically utilized to protect from the growth of fog in storage and to reduce image fading. Stabilizers are however expensive and not generally required for silver halide images attached to packages of the invention since the shelf life of a package tends to be less than one calendar year. Silver halide imaging layers substantially free of stabilizers would be low in cost and have acceptable image quality for images attached to packages.

[0130] Stabilizers and scavengers that can be used in these photographic elements, but are not limited to, the following:

25

30

35

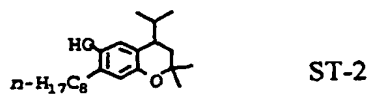
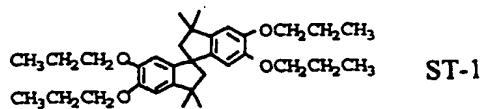
40

45

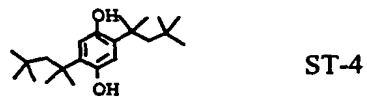
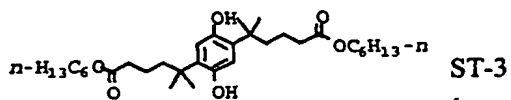
50

55

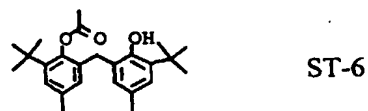
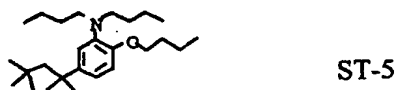
5



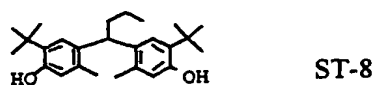
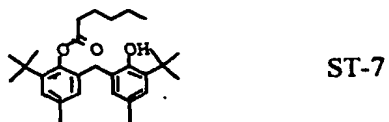
10



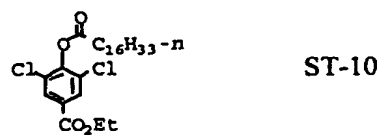
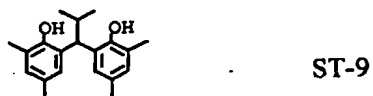
15



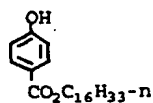
20



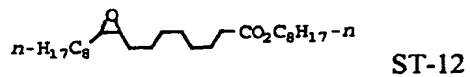
25



30



ST-11



35

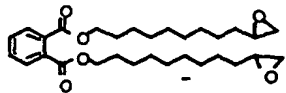
40

45

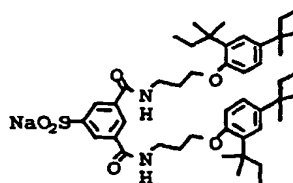
50

55

5

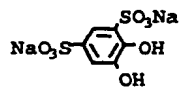


ST-13

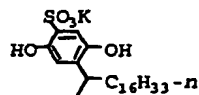


ST-14

10

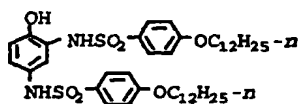


ST-15

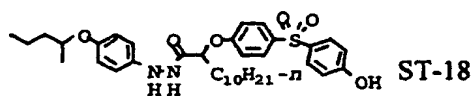


ST-16

15



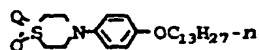
ST-17



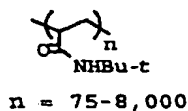
ST-18

20

25

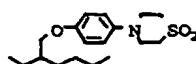


ST-19

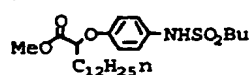


ST-20

30



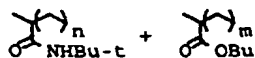
ST-21



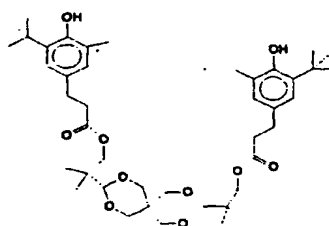
ST-22

35

40



ST-23



ST-24

45

n:m 1:1 mw = 75-100,000

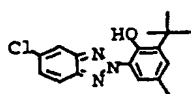
50

Examples of solvents which may be used in the invention include the following:

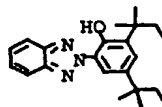
55

| | |
|---|------|
| Tritolyl phosphate | S-1 |
| Dibutyl phthalate | S-2 |
| Diundecyl phthalate | S-3 |
| <i>N,N</i> -Diethyldodecanamide | S-4 |
| <i>N,N</i> -Dibutyldodecanamide | S-5 |
| Tris(2-ethylhexyl)phosphate | S-6 |
| Acetyl tributyl citrate | S-7 |
| 2,4-Di- <i>tert</i> -pentylphenol | S-8 |
| 2-(2-Butoxyethoxy)ethyl acetate | S-9 |
| 1,4-Cyclohexyldimethylene bis(2-ethylhexanoate) | S-10 |

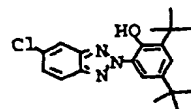
[0131] The dispersions used in photographic elements may also include ultraviolet (UV) stabilizers and so called liquid UV stabilizers such as described in U.S. Patent Nos. 4,992,358; 4,975,360; and 4,587,346. Examples of UV stabilizers are shown below.



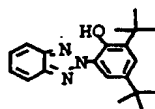
UV-1



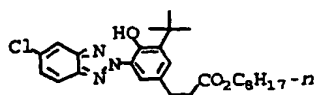
UV-2



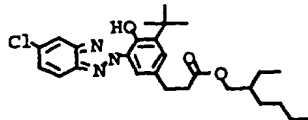
UV-3



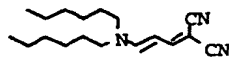
UV-4



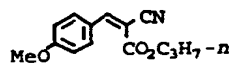
UV-5



UV-6

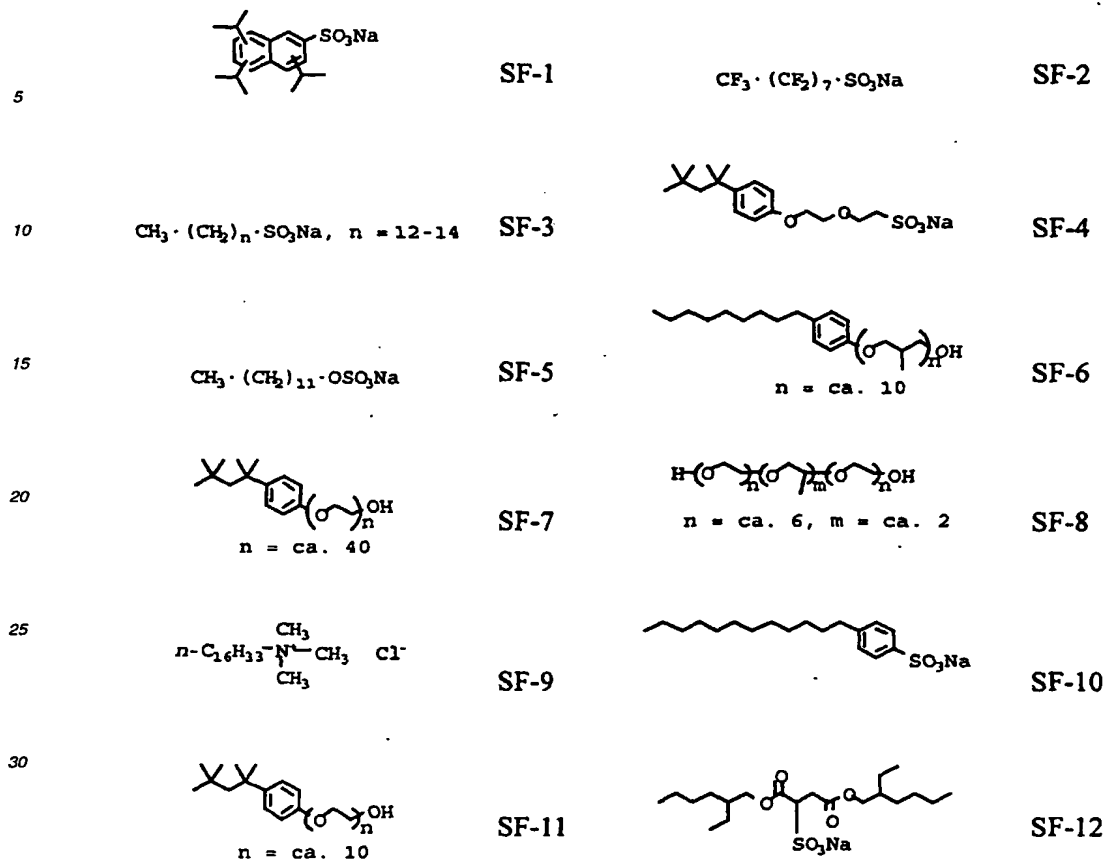


UV-7



UV-8

[0132] The aqueous phase may include surfactants. Surfactant may be cationic, anionic, zwitterionic or non-ionic. Useful surfactants include, but are not limited to, the following.



[0133] Further, it is contemplated to stabilize photographic dispersions prone to particle growth through the use of hydrophobic, photographically inert compounds such as disclosed by Zengerle et al in U.S. Patent 5,468,604.

[0134] In a preferred embodiment the invention employs recording elements which are constructed to contain at least three silver halide emulsion layer units. A suitable full color, multilayer format for a recording element used in the invention is represented by Structure I.

| |
|--|
| <div>5</div> <div>Red-sensitized</div> <div>cyan dye image-forming silver halide emulsion unit</div> |
| <div>Interlayer</div> |
| <div>10</div> <div>Green-sensitized</div> <div>magenta dye image-forming silver halide emulsion unit</div> |
| <div>Interlayer</div> |
| <div>15</div> <div>Blue-sensitized</div> <div>yellow dye image-forming silver halide emulsion unit</div> |
| <div>//// Support ////</div> |

STRUCTURE I

wherein the red-sensitized, cyan dye image-forming silver halide emulsion unit is situated nearest the support; next in order is the green-sensitized, magenta dye image-forming unit, followed by the uppermost blue-sensitized, yellow dye image-forming unit. The image-forming units are separated from each other by hydrophilic colloid interlayers containing an oxidized developing agent scavenger to prevent color contamination. Silver halide emulsions satisfying the grain and gelatino-peptizer requirements described above can be present in any one or combination of the emulsion layer units. Additional useful multicolor, multilayer formats for an element of the invention include structures as described in U.S. Patent 5,783,373. Each of such structures in accordance with the invention preferably would contain at least three silver halide emulsions comprised of high chloride grains having at least 50 percent of their surface area bounded by {100} crystal faces and containing dopants from classes (i) and (ii), as described above. Preferably each of the emulsion layer units contains emulsion satisfying these criteria.

[0135] Conventional features that can be incorporated into multilayer (and particularly multicolor) recording elements contemplated for use in the method of the invention are illustrated by *Research Disclosure*, Item 38957, cited above:

- XI. Layers and layer arrangements
- XII. Features applicable only to color negative
- XIII. Features applicable only to color positive

- B. Color reversal
- C. Color positives derived from color negatives

- XIV. Scan facilitating features.

[0136] The recording elements comprising the radiation sensitive high chloride emulsion layers according to this invention can be conventionally optically printed, or in accordance with a particular embodiment of the invention can be image-wise exposed in a pixel-by-pixel mode using suitable high energy radiation sources typically employed in electronic printing methods. Suitable actinic forms of energy encompass the ultraviolet, visible and infrared regions of the electromagnetic spectrum as well as electron-beam radiation and is conveniently supplied by beams from one or more light emitting diodes or lasers, including gaseous or solid state lasers. Exposures can be monochromatic, orthochromatic or panchromatic. For example, when the recording element is a multilayer multicolor element, exposure can be provided by laser or light emitting diode beams of appropriate spectral radiation, for example, infrared, red, green or blue wavelengths, to which such element is sensitive. Multicolor elements can be employed which produce cyan, magenta and yellow dyes as a function of exposure in separate portions of the electromagnetic spectrum, including at least two portions of the infrared region, as disclosed in the previously mentioned U.S. Patent No. 4,619,892. Suitable exposures include those up to 2000 nm, preferably up to 1500 nm. Suitable light emitting diodes and commercially

available laser sources are known and commercially available. Imagewise exposures at ambient, elevated or reduced temperatures and/or pressures can be employed within the useful response range of the recording element determined by conventional sensitometric techniques, as illustrated by T.H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, Chapters 4, 6, 17, 18 and 23.

5 [0137] It has been observed that anionic $[MX_xY_yL_z]$ hexacoordination complexes, where M is a group 8 or 9 metal (preferably iron, ruthenium or iridium), X is halide or pseudohalide (preferably Cl, Br or CN) x is 3 to 5, Y is H_2O , y is 0 or 1, L is a C-C, H-C or C-N-H organic ligand, and Z is 1 or 2, are surprisingly effective in reducing high intensity reciprocity failure (HIRF), low intensity reciprocity failure (LIRF) and thermal sensitivity variance and in improving latent image keeping (LIK). As herein employed HIRF is a measure of the variance of photographic properties for equal exposures, but with exposure times ranging from 10^{-1} to 10^{-6} second. LIRF is a measure of the variance of photographic properties for equal exposures, but with exposure times ranging from 10^{-1} to 100 seconds. Although these advantages can be generally compatible with face centered cubic lattice grain structures, the most striking improvements have been observed in high (>50 mole %, preferably ≥ 90 mole %) chloride emulsions. Preferred C-C, H-C or C-N-H organic ligands are aromatic heterocycles of the type described in U.S. Pat. No. 5,462,849. The most effective C-C, H-C or C-N-H organic ligands are azoles and azines, either unsubstituted or containing alkyl, alkoxy or halide substituents, where the alkyl moieties contain from 1 to 8 carbon atoms. Particularly preferred azoles and azines include thiazoles, thiazolines and pyrazines.

[0138] The quantity or level of high energy actinic radiation provided to the recording medium by the exposure source is generally at least 10^{-4} ergs/cm², typically in the range of about 10^{-4} ergs/cm² to 10^{-3} ergs/cm² and often from 10^{-3} ergs/cm² to 10^2 ergs/cm². Exposure of the recording element in a pixel-by-pixel mode as known in the prior art persists for only a very short duration or time. Typical maximum exposure times are up to 100 μ seconds, often up to 10 μ seconds, and frequently up to only 0.5 μ seconds. Single or multiple exposures of each pixel are contemplated. The pixel density is subject to wide variation, as is obvious to those skilled in the art. The higher the pixel density, the sharper the images can be, but at the expense of equipment complexity. In general, pixel densities used in conventional electronic printing methods of the type described herein do not exceed 10^7 pixels/cm² and are typically in the range of about 10^4 to 10^6 pixels/cm². An assessment of the technology of high-quality, continuous-tone, color electronic printing using silver halide photographic paper which discusses various features and components of the system, including exposure source, exposure time, exposure level and pixel density and other recording element characteristics is provided in Firth et al., *A Continuous-Tone Laser Color Printer*, Journal of Imaging Technology, Vol. 14, No. 3, June 1988, which is hereby incorporated herein by reference. As previously indicated herein, a description of some of the details of conventional electronic printing methods comprising scanning a recording element with high energy beams such as light emitting diodes or laser beams, are set forth in Hioki U.S. Patent 5,126,235, European Patent Applications 479 167 A1 and 502 508 A1.

[0139] Once imagewise exposed, the recording elements can be processed in any convenient conventional manner to obtain a viewable image. Such processing is illustrated by *Research Disclosure*, Item 38957, cited above:

XVIII. Chemical development systems

XIX. Development

XX. Desilvering, washing, rinsing and stabilizing

40 [0140] In addition, a useful developer for the inventive material is a homogeneous, single part developing agent. The homogeneous, single-part color developing concentrate is prepared using a critical sequence of steps:

[0141] In the first step, an aqueous solution of a suitable color developing agent is prepared. This color developing agent is generally in the form of a sulfate salt. Other components of the solution can include an antioxidant for the color developing agent, a suitable number of alkali metal ions (in an at least stoichiometric proportion to the sulfate ions) provided by an alkali metal base, and a photographically inactive water-miscible or water-soluble hydroxy-containing organic solvent. This solvent is present in the final concentrate at a concentration such that the weight ratio of water to the organic solvent is from about 15:85 to about 50:50.

[0142] In this environment, especially at high alkalinity, alkali metal ions and sulfate ions form a sulfate salt that is precipitated in the presence of the hydroxy-containing organic solvent. The precipitated sulfate salt can then be readily removed using any suitable liquid/solid phase separation technique (including filtration, centrifugation or decantation). If the antioxidant is a liquid organic compound, two phases may be formed and the precipitate may be removed by discarding the aqueous phase.

[0143] The color developing concentrates of this invention include one or more color developing agents that are well known in the art that, in oxidized form, will react with dye forming color couplers in the processed materials. Such color developing agents include, but are not limited to, aminophenols, *p*-phenylenediamines (especially *N,N*-dialkyl-*p*-phenylenediamines) and others which are well known in the art, such as EP 0 434 097A1 (published June 26, 1991) and EP 0 530 921A1 (published March 10, 1993). It may be useful for the color developing agents to have one or more

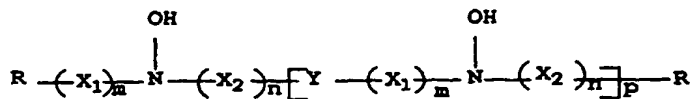
water-solubilizing groups as are known in the art. Further details of such materials are provided in *Research Disclosure*, publication 38957, pages 592-639 (September 1996). *Research Disclosure* is a publication of Kenneth Mason Publications Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ England (also available from Emsworth Design Inc., 121 West 19th Street, New York, N.Y. 10011). This reference will be referred to hereinafter as "*Research Disclosure*".

[0144] Preferred color developing agents include, but are not limited to, N,N-diethyl *p*-phenylenediamine sulfate (KODAK Color Developing Agent CD-2), 4-amino-3-methyl-N-(2-methanesulfonamidoethyl)aniline sulfate, 4-(N-ethyl-N-β-hydroxyethylamino)-2-methylaniline sulfate (KODAK Color Developing Agent CD-4), *p*-hydroxyethylethylaminoaniline sulfate, 4-(N-ethyl-N-2-methanesulfonamidoethyl)-2-methylphenylenediamine sesquisulfate (KODAK Color Developing Agent CD-3), 4-(N-ethyl-N-2-methanesulfonaminoethyl)-2-methylphenylenediamine sesquisulfate, and others readily apparent to one skilled in the art.

[0145] In order to protect the color developing agents from oxidation, one or more antioxidants are generally included in the color developing compositions. Either inorganic or organic antioxidants can be used. Many classes of useful antioxidants are known, including but not limited to, sulfites (such as sodium sulfite, potassium sulfite, sodium bisulfite and potassium metabisulfite), hydroxylamine (and derivatives thereof), hydrazines, hydrazides, amino acids, ascorbic acid (and derivatives thereof), hydroxamic acids, aminoketones, mono- and polysaccharides, mono- and polyamines, quaternary ammonium salts, nitroxyl radicals, alcohols, and oximes. Also useful as antioxidants are 1,4-cyclohexadienes. Mixtures of compounds from the same or different classes of antioxidants can also be used if desired.

[0146] Especially useful antioxidants are hydroxylamine derivatives as described for example, in US Patent Nos. 4,892,804, 4,876,174; 5,354,646; and 5,660,974, all noted above, and 5,646,327 (Burns et al). Many of these antioxidants are mono- and dialkylhydroxylamines having one or more substituents on one or both alkyl groups. Particularly useful alkyl substituents include sulfo, carboxy, amino, sulfonamido, carbonamido, hydroxy and other solubilizing substituents.

[0147] More preferably, the noted hydroxylamine derivatives can be mono- or dialkylhydroxylamines having one or more hydroxy substituents on the one or more alkyl groups. Representative compounds of this type are described, for example, in U.S. Patent 5,709,982 (Marrese et al), as having the structure I:



wherein R is hydrogen, a substituted or unsubstituted alkyl group of 1 to 10 carbon atoms, a substituted or unsubstituted hydroxyalkyl group of 1 to 10 carbon atoms, a substituted or unsubstituted cycloalkyl group of 5 to 10 carbon atoms, or a substituted or unsubstituted aryl group having 6 to 10 carbon atoms in the aromatic nucleus.

[0148] X_1 is $-\text{CR}_2(\text{OH})\text{CHR}_1-$ and X_2 is $-\text{CHR}_1\text{CR}_2(\text{OH})-$ wherein R_1 and R_2 are independently hydrogen, hydroxy, a substituted or unsubstituted alkyl group or 1 or 2 carbon atoms, a substituted or unsubstituted hydroxyalkyl group of 1 or 2 carbon atoms, or R_1 and R_2 together represent the carbon atoms necessary to complete a substituted or unsubstituted 5- to 8-membered saturated or unsaturated carbocyclic ring structure.

[0149] Y is a substituted or unsubstituted alkylene group having at least 4 carbon atoms, and has an even number of carbon atoms, or Y is a substituted or unsubstituted divalent aliphatic group having an even total number of carbon and oxygen atoms in the chain, provided that the aliphatic group has at least 4 atoms in the chain.

[0150] Also in Structure I, m, n and p are independently 0 or 1. Preferably, each of m and n is 1, and p is 0.

[0151] Specific di-substituted hydroxylamine antioxidants include, but are not limited to: N,N-bis(2,3-dihydroxypropyl)hydroxylamine, N,N-bis(2-methyl-2,3-dihydroxypropyl)hydroxylamine and N,N-bis(1-hydroxymethyl-2-hydroxy-3-phenylpropyl)hydroxylamine. The first compound is preferred.

[0152] The colorants can be incorporated into the imaging element by direct addition of the colorant to a coating melt by mixing the colorant with an aqueous medium containing gelatin (or other hydrophilic colloid) at a temperature of 40°C or higher. The colorant can also be mixed with an aqueous solution of a water-soluble or water-dispersible surfactant or polymer, and passing the premix through a mill until the desired particle size is obtained. The mill can be any high energy device such as a colloid mill, high pressure homogenizer, or the like.

[0153] The preferred color of the pigment is blue as a blue pigment incorporated into a gelatin layer offsets the native yellowness of the gelatin yielding a neutral background for the image layers.

[0154] Suitable pigments used in this invention can be any inorganic or organic, colored materials which are practically insoluble in the medium in which they are incorporated. The preferred pigments are organic, and are those described in *Industrial Organic Pigments: Production, Properties, Applications* by W. Herbst and K. Hunger, 1993, Wiley

Publishers. These include: Azo Pigments such as monoazo yellow and orange, diazo, naphthol, naphthol reds, azo lakes, benzimidazolone, disazo condensation, metal complex, isoindolinone and isoindoline, Polycyclic Pigments such as phthalocyanine, quinacridone, perylene, perinone, diketopyrrolo pyrrole and thioindigo, and Anthraquinone Pigments such as anthrapyrimidine, flavanthrone, pyranthrone, anthanthrone, dioxazine, triarylcarbodium and quinophthalone.

5 [0155] The most preferred pigments are the anthraquinones such as Pigment Blue 60, phthalocyanines such as Pigment Blue 15, 15:1, 15:3, 15:4 and 15:6, and quinacridones such as Pigment Red 122, as listed in NPIRI Raw Materials Data Handbook, Vol. 4, Pigments, 1983, National Printing Research Institute. These pigments have a dye hue sufficient to overcome the native yellowness of the gelatin imaging layer and are easily dispersed in a aqueous solution.

10 [0156] An aqueous dispersion of the pigments is preferred because the preferred pigments are insoluble in most, if not all, organic solvents, and therefore a high quality dispersion is not likely in a solvent system. In fact, the only solvent that will dissolve preferred pigments PR-122 and PB-15 is concentrated sulfuric acid, which is not an organic solvent. Preferred pigments of the invention are by nature, insoluble, crystalline solids, which is the most thermodynamically stable form that they can assume. In an oil and water dispersion, they would be in the form of an amorphous solid, which is thermodynamically unstable. Therefore, one would have to worry about the pigment eventually converting to the crystalline form with age. We might as well start with a crystalline solid and not worry about preventing the phase transition. Another reason to avoid solvent pigment dispersions is that the high boiling solvent is not removed with evaporation, and it could cause unwanted interactions in the coating melt such as ripening of DOH dispersion particles, or equilibration with other layers, if it was used in the coating. The use of solid particle dispersion avoids organic solvents altogether.

20 [0157] In the preferred embodiment, the colorant is dispersed in the binder in the form of a solid particle dispersion. Such dispersions are formed by first mixing the colorant with an aqueous solution containing a water-soluble or water-dispersible surfactant or polymer to form a coarse aqueous premix, and adding the premix to a mill. The amount of water-soluble or water-dispersible surfactant or polymer can vary over a wide range, but is generally in the range of 0.01% to 100% by weight of polymer, preferably about 0.3% to about 60%, and more preferably 0.5% to 50%, the percentages being by weight of polymer, based on the weight of the colorant useful in imaging.

25 [0158] The mill can be, for example, a ball mill, media mill, attritor mill, vibratory mill or the like. The mill is-charged with the appropriate milling media such as, for example, beads of silica, silicon nitride, sand, zirconium oxide, yttria-stabilized zirconium oxide, alumina, titanium, glass, polystyrene, etc. The bead sizes typically range from 0.25 to 3.0 mm in diameter, but smaller media can be used if desired. The premix is milled until the desired particle size range is reached.

30 [0159] The solid colorant particles are subjected to repeated collisions with the milling media, resulting in crystal fracture, deagglomeration, and consequent particle size reduction. The solid particle dispersions of the colorant should have a final average particle size of less than 1 micrometers, preferably less than 0.1 micrometers, and most preferably between 0.01 and 0.1 micrometers. Most preferably, the solid colorant particles are of sub-micrometer average size. Solid particle size between 0.01 and 0.1 provides the best pigment utilization and had a reduction in unwanted light absorption compared to pigments with a particle size greater than 1.2 micrometers.

35 [0160] The preferred gelatin to pigment ratio in any gelatin layer is between 65,000:1 to 195,000:1. This gelatin to pigment ratio is preferred as this range provides the necessary color correction to typical photographic imaging layers and typical ink jet dye receiving layers to provide a perceptually preferred neutral background in the image. The preferred coverage of pigment in the gelatin layer is between 0.006 grams/m² and 0.020 grams/m². Coverages less than 0.006 gram/m² are not sufficient to provide proper correction of the color and coverages greater than 0.025 grams/m² yield a density minimum that has been found to be objectionable by consumers.

40 [0161] Surfactants, polymers, and other additional conventional addenda may also be used in the dispersing process described herein in accordance with prior art solid particle dispersing procedures. Such surfactants, polymers and other addenda are disclosed in U.S. Pat. Nos. 5,468,598; 5,300,394; 5,278,037; 4,006,025; 4,924,916; 4,294,917; 4,940,654; 4,950,586; 4,927,744; 5,279,931; 5,158,863; 5,135,844; 5,091,296; 5,089,380; 5,103,640; 4,990,431; 4,970,139; 5,256,527; 5,089,380; 5,103,640; 4,990,431; 4,970,139; 5,256,527; 5,015,564; 5,008,179; 4,957,857; and 2,870,012, British Patent specifications Nos. 1,570,362 and 1,131,179 in the dispersing process of the colorants.

45 [0162] Additional surfactants or other water soluble polymers may be added after formation of the colorant dispersion, before or after subsequent addition of the colorant dispersion to an aqueous coating medium for coating onto an imaging element support. The aqueous medium preferably contains other compounds such as stabilizers and dispersants, for example, additional anionic, nonionic, zwitterionic, or cationic surfactants, and water soluble binders such as gelatin as is well known in the imaging art. The aqueous coating medium may further contain other dispersions or emulsions of compounds useful in imaging.

50 [0163] The following examples illustrate the practice of this invention. They are not intended to be exhaustive of all possible variations of the invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLES

Example 1

5 [0164] In this example a silver halide packaging label was created by coating light sensitive silver halide imaging layers on a flexible, transparent polyester sheet that contained an integral polyethylene layer used to promote silver halide emulsion adhesion to the flexible, transparent polymer sheet. After developing the image, the photographic label was laminated to an opaque, white, tough polypropylene base sheet utilizing a pressure sensitive adhesive. This example will demonstrate the numerous advantages that a silver halide packaging label has compared to typical prior art
10 rotogravure printed labels.

Flexible, transparent polyester sheet:

15 [0165] An oriented polyethylene terephthalate transparent sheet with a thickness of 37 micrometers. The polyethylene terephthalate base had a stiffness of 15 millinewtons in the machine direction and 20 millinewtons in the cross direction. The transparent polyester sheet had a low density polyethylene skin layer that was 1 micrometer thick and contained blue pigments to offset the native yellowness of the gelatin used in the silver halide imaging layers.

Biaxially oriented base sheet:

20 [0166] An oriented three layer composite sheet polyolefin sheet (31 micrometers thick) ($d = 0.68$ g/cc) consisting of a microvoided and oriented polypropylene core (approximately 60% of the total sheet thickness), with a homopolymer non-microvoided oriented polypropylene layer on each side of the voided layer; the void initiating material used was poly(butylene terephthalate). The polypropylene layer adjacent the voided layer contained TiO_2 and optical brightener.

25 Pressure sensitive adhesive:

Permanent water based acrylic adhesive 12 micrometers thick

30 [0167] Silver chloride emulsions were chemically and spectrally sensitized as described below. A biocide comprising a mixture of N-methyl-isothiazolone and N-methyl-5-chloro-isthiazolone was added after sensitization.

[0168] **Blue Sensitive Emulsion (Blue EM-1).** A high chloride silver halide emulsion is precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing glutaryldiaminophenyldisulfide, gelatin peptizer, and thioether ripener. Cesium pentachloronitrosylsulfate(II) dopant is added during
35 the silver halide grain formation for most of the precipitation, followed by the addition of potassium hexacyanoruthenate(II), potassium (5-methylthiazole)-pentachloroiridate, a small amount of KI solution, and shelling without any dopant. The resultant emulsion contains cubic shaped grains having edge length of $0.6\mu\text{m}$. The emulsion is optimally sensitized by the addition of a colloidal suspension of aurous sulfide and heat ramped to 60°C , during which time blue sensitizing dye BSD-4, potassium hexachloroiridate, Lippmann bromide, and 1-(3-acetamidophenyl)-5-mercaptotetrazole were
40 added.

[0169] **Green Sensitive Emulsion (Green EM-1):** A high chloride silver halide emulsion is precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. Cesium pentachloronitrosylsulfate(II) dopant is added during the silver halide grain formation for most of the precipitation, followed by the addition of potassium (5-methylthiazole)-pentachloroiridate. The
45 resultant emulsion contains cubic shaped grains of $0.3\mu\text{m}$ in edge length size. The emulsion is optimally sensitized by the addition of glutaryldiaminophenyldisulfide, a colloidal suspension of aurous sulfide and heat ramped to 55°C , during which time potassium hexachloroiridate doped Lippmann bromide, a liquid crystalline suspension of green sensitizing dye GSD-1, and 1-(3-acetamidophenyl)-5-mercaptotetrazole were added.

[0170] **Red Sensitive Emulsion (Red EM-1):** A high chloride silver halide emulsion is precipitated by adding approximately equimolar silver nitrate and sodium chloride solutions into a well-stirred reactor containing gelatin peptizer and thioether ripener. During the silver halide grain formation, potassium hexacyanoruthenate(II) and potassium (5-methylthiazole)-pentachloroiridate are added. The resultant emulsion contains cubic shaped grains of $0.4\mu\text{m}$ in
50 edge length size. The emulsion is optimally sensitized by the addition of glutaryldiaminophenyldisulfide, sodium thiosulfate, tripotassium bis(2-[3-(2-sulfobenzamido)phenyl]mercaptotetrazole) gold(I) and heat ramped to 64°C , during which time 1-(3-acetamidophenyl)-5-mercaptotetrazole, potassium hexachloroiridate, and potassium bromide are added. The
55 emulsion is then cooled to 40°C , pH adjusted to 6.0, and red sensitizing dye RSD-1 is added.

[0171] Coupler dispersions were emulsified by methods well known to the art, and the following layers were coated on the following support:

[0172] The following light sensitive silver halide imaging layers were utilized to prepare photographic label utilizing the invention label support material. The following imaging layers were coated utilizing curtain coating:

| Layer | Item | Laydown (g/m ²) |
|----------------|---|-----------------------------|
| Layer 1 | Blue Sensitive Layer | |
| | Gelatin | 1.3127 |
| | Blue sensitive silver (Blue EM-1) | 0.2399 |
| | Y-4 | 0.4143 |
| | ST-23 | 0.4842 |
| | Tributyl Citrate | 0.2179 |
| | ST-24 | 0.1211 |
| | ST-16 | 0.0095 |
| | Sodium Phenylmercaptotetrazole | 0.0001 |
| | Piperidino hexose reductone | 0.0024 |
| | 5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1) | 0.0002 |
| | SF-1 | 0.0366 |
| | Potassium chloride | 0.0204 |
| | Dye-1 | 0.0148 |
| Layer 2 | Interlayer | |
| | Gelatin | 0.7532 |
| | ST-4 | 0.1076 |
| | S-3 | 0.1969 |
| | 5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1) | 0.0001 |
| | Catechol disulfonate | 0.0323 |
| | SF-1 | 0.0081 |
| Layer 3 | Green Sensitive Layer | |
| | Gelatin | 1.1944 |
| | Green Sensitive Silver (Green EM-1) | 0.1011 |
| | M-4 | 0.2077 |
| | Oleyl Alcohol | 0.2174 |
| | S-3 | 0.1119 |
| | ST-21 | 0.0398 |
| | ST-22 | 0.2841 |
| | Dye-2 | 0.0073 |
| | 5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1) | 0.0001 |
| | SF-1 | 0.0236 |
| | Potassium chloride | 0.0204 |
| | Sodium Phenylmercaptotetrazole | 0.0007 |
| Layer 4 | M/C Interlayer | |
| | Gelatin | 0.7532 |
| | ST-4 | 0.1076 |
| | S-3 | 0.1969 |

| | | |
|----|---|--------|
| | Acrylamide/t-Butylacrylamide sulfonate copolymer | 0.0541 |
| | Bis-vinylsulfonylmethane | 0.1390 |
| 5 | 3,5-Dinitrobenzoic acid | 0.0001 |
| | Citric acid | 0.0007 |
| | Catechol disulfonate | 0.0323 |
| | 5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1) | 0.0001 |
| 10 | Layer 5 Red Sensitive Layer | |
| | Gelatin | 1.3558 |
| | Red Sensitive silver (Red EM-1) | 0.1883 |
| 15 | IC-35 | 0.2324 |
| | IC-36 | 0.0258 |
| | UV-2 | 0.3551 |
| | Dibutyl sebacate | 0.4358 |
| 20 | S-6 | 0.1453 |
| | Dye-3 | 0.0229 |
| | Potassium p-toluenethiosulfonate | 0.0026 |
| 25 | 5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1) | 0.0001 |
| | Sodium Phenylmercaptotetrazole | 0.0005 |
| | SF-1 | 0.0524 |
| | Layer 6 UV Overcoat | |
| 30 | Gelatin | 0.8231 |
| | UV-1 | 0.0355 |
| | UV-2 | 0.2034 |
| | ST-4 | 0.0655 |
| 35 | SF-1 | 0.0125 |
| | S-6 | 0.0797 |
| | 5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1) | 0.0001 |
| 40 | Layer 7 SOC | |
| | Gelatin | 0.6456 |
| | Ludox AM™ (colloidal silica) | 0.1614 |
| | Polydimethylsiloxane (DC200™) | 0.0202 |
| 45 | 5-chloro-2-methyl-4-isothiazolin-3-one/2-methyl-4-isothiazolin-3-one(3/1) | 0.0001 |
| | SF-2 | 0.0032 |
| | Tergitol 15-S-5™ (surfactant) | 0.0020 |
| 50 | SF-1 | 0.0081 |
| | Aerosol OT™ (surfactant) | 0.0029 |

[0173] The silver halide imaging layers described above were applied to the polyethylene shin layer of the transparent polymer sheet using curtain coating. Structure of the photographic packaging label material of the example after

application of the silver halide imaging layers was as follows:

| | |
|---|---|
| 5 | Oriented polyester |
| | <hr/> |
| | Oriented polyethylene with blue tint (1 micrometer) |
| | <hr/> |
| | Silver halide imaging layers of the example |

10 [0174] The 10 mm slit rolls of light sensitive silver halide emulsion coated label support of this example was reverse printed using a digital CRT photographic printer. Several test images were printed on the photographic label material. The test images contained text, graphics, and images of people. The printed images were then developed using standard reflective RA 4 photographic wet chemistry. At this point, the developed silver halide image was formed on a thin
15 label support. To further improve the durability of the developed image layers, an opaque label base material was laminated to the silver halide imaging layers utilizing a pressure sensitive acrylic adhesive. The structure of the printed, over laminated photographic label was as follows:

| | |
|----|---|
| 20 | Oriented polyester |
| | <hr/> |
| | Oriented polyethylene with blue tint (1 micrometer) |
| | <hr/> |
| | Silver halide imaging layers |
| 25 | <hr/> |
| | Acrylic pressure sensitive adhesive |
| | <hr/> |
| | Polypropylene with 8% rutile TiO ₂ |
| | <hr/> |
| | Oriented, voided polypropylene |
| 30 | <hr/> |
| | Polypropylene |

[0175] The above imaged opaque photographic label material was hand applied to several PET beverage bottles utilizing a standard pressure sensitive adhesive.

35 [0176] The photographic label of the invention showed many significant improvements compared to prior art lower in quality flexography or gravure printed labels. The invention provides a printing method that is economically viable when printing short runs as the cost of printing plates or printing cylinders are avoided. Because a digital silver halide imaging system was used to print the labels, each label can be different without the need for expensive printing press setup costs. The use of silver halide images applied to a package ensures the highest image quality currently available
40 compared to lower quality six color rotogravure printed labels. The delicate developed silver halide imaging layers are protected from water, handling damage, and scratches by a tough base sheet laminated to the silver halide imaging layers. Further, because the yellow, magenta, and cyan layers contain gelatin interlayers, the silver halide images appear to have depth compared to ink jet, electrophotographic, or gravure printed images which appear flat and lifeless. The silver halide image layers of the invention have also been optimized to accurately replicate flesh tones, providing superior images of people compared to alternate digital imaging technologies.

45 [0177] Silver halide image technology utilized in the example can simultaneously print text, graphics, and photographic quality images on the same package. Since the silver halide imaging layers of the invention are digitally compatible, text, graphics and images can be printed using known digital printing equipment such as lasers and CRT printers. Because the silver halide system is digitally compatible, each package can contain different data enabling customization of individual packages without the extra expense of printing plates or cylinders. Further, printing digital files
50 allows the files to be transported using electronic data transfer technology such as the internet, thus reducing the cycle time to apply printing to a package. The silver halide imaging layers of the example can also be digitally exposed with a laser or CRT at speeds greater than 75 meters per minute, allowing competitive printing speeds compared to current ink jet or electrophotographic digital printing engines.

55 [0178] Finally, the photographic label format of the invention allows for the label to be utilized in high speed packaging equipment, as great care was taken to ensure that the tensile strength and coefficient properties of the flexible, transparent polymer sheet, and the base sheet were within the operating ranges of high speed packaging equipment. Lamination of the developed silver halide imaging layers to the base sheet of the invention also provided excellent pro-

tection against handling damage and water spots. Unexpectedly, the encapsulated light sensitive silver halide imaging layers had exceptional dye fade performance, which could allow for the reduction of image stabilizer compounds in the silver halide imaging layers.

5 Claims

1. An element consisting essentially of a transparent polymer sheet, at least one emulsion adhering layer, and at least one light sensitive silver halide grain containing emulsion layer adhered to said emulsion adhering layer, wherein said polymer sheet is less than 40 μm in thickness.
2. The element of Claim 1 wherein said transparent polymer sheet comprises at least one polymer selected from the group consisting of polyolefins, polyesters, polyamides, polycarbonates, cellulosic esters, polystyrene, polyvinyl resins, polysulfonamides, polyethers, polyimides, polyvinylidene fluoride, polyurethanes, polyphenylenesulfides, polytetrafluoroethylene, polyacetals, polysulfonates, polyester ionomers, and polyolefin ionomers.
3. The element of Claim 2 wherein said transparent polymer sheet comprises polyester.
4. The element of Claim 1 wherein said transparent polymer sheet comprises a polyolefin polymer.
5. The element of any of Claims 1 to 4 wherein the thickness of said polymer sheet is between 10 and 20 μm .
6. The element of any of Claims 1 to 6 wherein said element is not provided with a protective layer over said at least one emulsion layer.
7. A covering material comprising an element consisting essentially of a transparent polymer sheet, at least one emulsion adhering layer, and at least one light sensitive silver halide grain containing emulsion layer adhered to said emulsion adhering layer, wherein said polymer sheet is less than 40 μm in thickness, an adhesive layer in contact with said at least one light sensitive silver halide grain containing emulsion layer, and a base sheet adhered to said adhesive layer.
8. The covering material of Claim 7 wherein said base material comprises a polymer sheet of a thickness of less than 100 μm .
9. The covering material of Claims 7 or 8 wherein said base material comprises an opaque polymer sheet having an optical transmission of less than 25 percent.
10. The covering material of any of Claims 7 to 9 wherein said element is substantially free of ultraviolet absorbing agents.
11. The covering material of any of Claims 7 to 10 wherein said element is substantially free of antihalation materials.
12. The covering material of any of Claims 7 to 11 wherein said transparent polymer sheet has a coefficient of friction of between 0.2 and 0.6.
13. A method of forming a covering material comprising providing an element consisting essentially of a transparent polymer sheet, at least one emulsion adhering layer, and at least one light sensitive silver halide grain containing emulsion layer adhered to said emulsion adhering layer, wherein said polymer sheet is less than 40 μm in thickness, imaging said at least one light sensitive silver halide grain containing emulsion layer, developing an image in said layer, and adhesively applying a base sheet to the developed image.

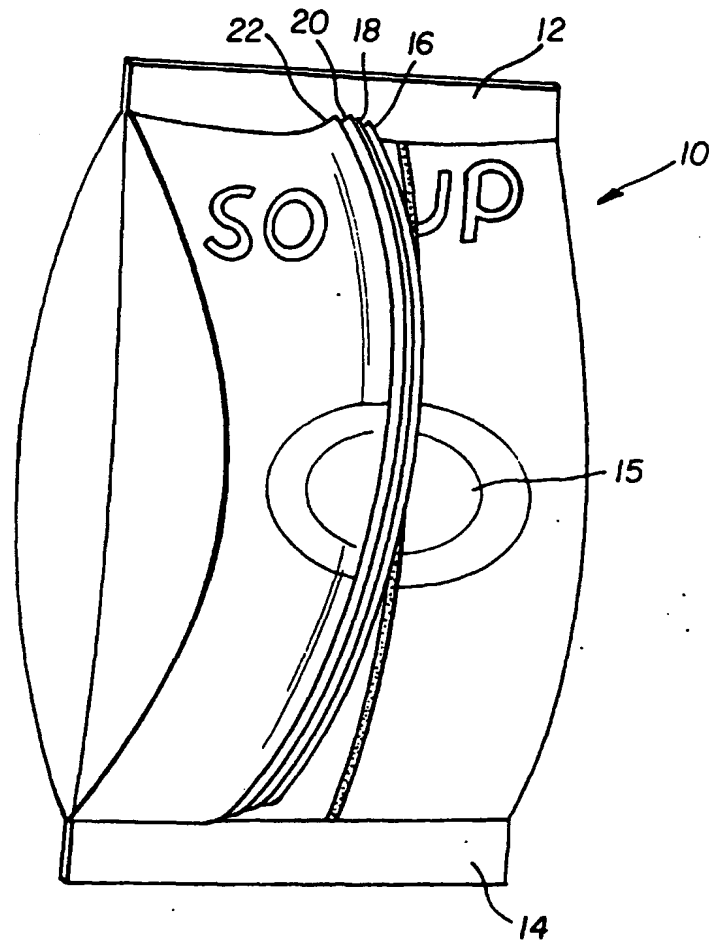


FIG. 1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 20 3195

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|--|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) |
| X | EP 0 007 048 A (CIBA-GEIGY) 23 January 1980 (1980-01-23) | 1-5, 7-11,13 | G03C11/14 G03C11/08 |
| Y | * page 3, line 28 - page 4, line 6 * * page 5, line 8 - page 7, line 16 * * page 9, line 1 - line 19; claims 6,7; figure 4 * | 6,12 | |
| Y | DE 15 97 642 A (TURAPHOT) 10 September 1970 (1970-09-10) * page 2, line 1 - line 8 * * page 3, line 1 - line 13 * * page 3, line 20 - line 27; claim 7 * | 6 | |
| Y | EP 0 915 373 A (KODAK) 12 May 1999 (1999-05-12) * page 7, line 40 - page 9, line 30 * | 12 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.7) |
| | | | G03C |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 12 October 2000 | Examiner Magrizos, S |
| CATEGORY OF CITED DOCUMENTS | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | | |

EPO FORM 1503 (03.02) (P4/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 20 3195

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

12-10-2000

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| EP 7048 A | 23-01-1980 | AT 392 T | 15-11-1981 |
| | | CA 1143990 A | 05-04-1983 |
| | | DE 2961310 D | 14-01-1982 |
| | | ES 482270 A | 16-02-1980 |
| | | JP 55015196 A | 02-02-1980 |
| | | US 4296198 A | 20-10-1981 |
| | | US 4355099 A | 19-10-1982 |
| | | ZA 7903390 A | 25-06-1980 |
| DE 1597642 A | 10-09-1970 | NONE | |
| EP 915373 A | 12-05-1999 | US 5965304 A | 12-10-1999 |
| | | JP 11218886 A | 10-08-1999 |

EPO FORM P449

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)